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Ground states of two-dimensional polyampholytes

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We perform an exact enumeration study of polymers formed from a (quenched) random sequence of charged monomers $\pm q_0$, restricted to a two-dimensional square lattice. Monomers interact via a logarithmic (Coulomb) interaction. We study the ground-state properties of the polymers as a function of their excess charge Q for all possible charge sequences up to a polymer length $N=18$. We find that the ground state of the neutral ensemble is compact and its energy extensive and self-averaging. The addition of a small excess charge causes an expansion of the ground state with the monomer density depending only on Q. In an annealed ensemble the ground state is fully stretched for any excess charge $Q>0$. [S1063-651X(97)07711-8]

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I. INTRODUCTION

Polymer systems have been subject to extensive study for several decades [1–3]. The interest in such macromolecules arises from many sources, where one important reason is the natural occurrence of polymers in biological systems, for example, proteins. Random polymers are also good examples of disordered systems, sharing common features with other physical systems exhibiting randomness or frustration [4,5]. An important class of polymers are *polyampholytes* (PAs), where the chain is composed of positively and negatively charged monomers [6]. Certain properties of proteins, some of whose constituents, the amino acids, may be charged [7], may be understood by studying PAs.

Much attention has been devoted to studying the ground-state properties of polymers (or the *native state* of proteins) and understanding which features determine their shape [4,5]. In PAs, the long-range Coulomb interaction between the monomers may, in the absence of screening, control the size and shape of the polymer, dominating over other short-range interactions. For $d>4$, the behavior of the PA is similar to that of random chains with short-range interactions, the Coulomb interaction becoming an irrelevant perturbation [8]. For $d<4$, the effect of the Coulomb interaction is complicated. Higgs and Joanny [9] and Wittemer *et al.* [10], expanding on arguments previously made by Edwards *et al.* [11], pointed out, on the basis of the Debye-Hückel theory [12], that charge fluctuations along the chain induce a net attractive interaction between segments of the chain, leading to a collapse of the PA to a compact shape. The resulting picture is of a *globule* consisting of densely packed *blobs*. Each blob is a dilute region of a weakly perturbed self-avoiding walk (SAW) of the size of the Debye-Hückel screening length. Lowering the temperature decreases the size of the blobs. This behavior is not a phase transition but rather a gradual increase of density of monomers with decreasing temperature. Charge correlations along the polymer may change the nature of the collapse [10]: A polymer with a quenched sequence of alternating charges will undergo a θ transition [13], like polymers with a short-range attraction interaction [14].

The application of the Debye-Hückel theory requires the strict neutrality of the system [12]. If we assign to each monomer along the chain a charge $q_i=\pm q_0$, then an excess charge $Q=\Sigma_{i=1}^{N}q_i$ may be defined. A random PA will not necessarily be neutral but may carry an excess charge Q, typically on the order of $q_0\sqrt{N}$. Gutin and Shakhnovich [15] and Dobrynin and Rubinstein [16] treated the problem of a charged PA. They found an expansion of the ground state due to an excess charge and describe it in the terms of an elongated globule with a Q-dependent aspect ratio. Observing that for neutral quenches $(Q=0)$ the ground state is compact, Kantor and Kardar [17–19] described the ground-state properties of a charged PA in an analogy to a drop of a fluid with a charge distributed in it: The energy of a neutral drop may be described by an extensive form with a surface tension accounting for the compact spherical shape. The excess charge Q is the important parameter determining the properties of the drop (or compact PA). A phenomenological description of the energy is given by

$$E=-\epsilon_c V+\gamma S+Q^2F(R), \tag{1}$$

where the first term is the extensive contribution to the energy (proportional to the volume V), the second term is a correction proportional to the surface area S, and the third term is the Coulomb interaction, where $F(R)$ represents the dependence of the Coulomb potential on the linear size of the drop R and is given (up to dimensionless prefactors of order unity) by

$$F(R)=\begin{cases}\dfrac{1}{R^{d-2}} & \text{for } d\neq 2\\ -\ln R & \text{for } d=2.\end{cases} \tag{2}$$

Increasing the charge Q creates an outward pressure that seeks to expand the drop, competing with the surface tension. At a certain excess charge, called the Rayleigh charge Q_R, the pressure difference between the inside and outside of the drop vanishes and the drop becomes locally unstable to elongation. In a d-dimensional PA this happens at $Q_R^2\approx q_0^2N^{2-3/d}$ [18]. However, even at a lower excess charge it might be energetically favorable to split a drop into two distant droplets, each carrying half the excess charge leading to a global instability. The critical charge Q_c when this occurs is found to be $Q_c^2=\alpha Q_R^2$, where the proportionality constant depends on d. This is the excess charge above which the PA should expand. In three dimensions, both the typical excess charge and the critical charge scale as $\sqrt{N}$; hence a typical PA will be stretched. Numerical studies using Monte Carlo methods [17] and exact enumeration techniques [18] support these qualitative predictions in three dimensions. Once the critical charge is exceeded, the PA expands, but it does not have the freedom of the drop to disintegrate since the polymer is a connected object. It can, however, be approximately described as a *necklace* [17] of weakly charged globules connected by highly charged strands of a PA.

While the three-dimensional (3D) case is important from the practical point of view, certain aspects cause conceptual difficulties (and consequently difficulties in the interpretation of Monte Carlo results). In three dimensions, both Q_R and the critical charge that determines the high-temperature behavior of a PA [8] and the typical fluctuation of the excess charge Q between the quenches have the same scaling: All three quantities are proportional to $\sqrt{N}$. It is therefore beneficial to study PAs in other space dimensions d. We study a model of a PA, a 2D randomly charged SAW on a 2D square lattice. Although this model significantly simplifies the complexity of real physical systems, we hope to gain some physical insight and understand the relevant mechanisms governing the behavior of the system. In Sec. II we elaborate on the specific model we study.

The logarithmic behavior of a 2D Coulomb potential creates difficulties that are absent in $d>2$: It is even not self-evident that the low-temperature configurations have an extensive energy and surface tension, i.e., that the description of Eq. (1) is applicable in two dimensions. In Sec. III we will show that the extensive description of the energy applies to our 2D model for $Q=0$. In Secs. IV and V we study the effect of excess charge on 2D PAs. Although the short chains studied prevent the verification of the necklace description, we see that any deviation from neutrality leads to an expansion of the ground state. We find that the system is much more susceptible to excess charge in two dimensions than in three dimensions.

II. MODEL AND METHOD

We model the polymer as a SAW on a 2D square lattice of spacing a. Monomer i along the chain has a charge q_i that is randomly assigned a value $\pm q_0$. The charges interact via a 2D Coulomb potential

$$E=-\sum_{\langle ij\rangle} q_i q_j \ln\frac{r_{ij}}{r_0}, \tag{3}$$

where r_{ij} is the distance between the ith and jth monomers and r_0 is an arbitrary constant setting the reference point of the energy. The study of a 2D system allows us to extend our study to longer polymers than was possible in three dimensions [18]. In addition, for short 2D chains, the surface to volume ratio, responsible for many of the properties of the polymer, is similar to that of long, realistic 3D chains [20]. Everywhere (except Sec. V), we consider a fixed charge sequence, i.e., quenched disorder. Note that the energy (3) is symmetric under charge conjugation, so we study only overall neutral and positively charged quenches.

In this study we apply the complete enumeration method: We create all possible spatial configurations of the chain and calculate exact quantities for each configuration. This allows us to find the ground state of the system and, when studying higher temperatures (results we do not report here), to compute exact thermodynamic averages. While the number of SAWs grows exponentially with N [2], limiting us to relatively short chains, this is the only method for studying exact ground-state properties since Monte Carlo methods fail to equilibrate at low temperatures. Up to $N=18$ we enumerated all possible charge sequences. For a PA 18 monomers long, after taking into account basic symmetries, there are 5 808 335 spatial configurations for each of the 77 819 possible quenches (unrelated by symmetry). Enumerating all configurations for all the quenches of $N=18$ required approximately 20 days of CPU time on a Silicon Graphics R10000 workstation. Up to a length of 26 monomers we enumerated only partial samples of all possible quenches (1000, 500, 100, and 50 random neutral quenches for lengths $N=20$, 22, 24, and 26, respectively). A 26-monomer-long chain has 15 435 169 364 possible spatial configurations, unrelated by symmetry. A similar model and method were employed by Kantor and Kardar [18] to study 3D systems up to $N=13$.

There is an important point to note regarding the energy of a 2D system with a fixed number of charges. We may express the distances as $r_{ij}=ar'_{ij}$, where r'_{ij} is a dimensionless distance (in lattice constants), and rewrite Eq. (3) in the form

$$E=-\sum_{\langle ij\rangle} q_i q_j \ln r'_{ij}-\frac{1}{2}(Q^2-q_0^2N)\ln\frac{a}{r_0}. \tag{4}$$

The first term depends on the specific spatial conformation. The second term is a constant reference point, independent of the spatial configuration or charge sequence along the polymer, and is a function of the excess charge only. Henceforth, we take $r_0=a$, so that the second term vanishes, and calculate only the first term as the ''energy.'' Within an ensemble of the same excess charge, this has no effect since we are interested only in energy differences. However, it must be kept in mind that for different excess charges and lengths, the choice of r_0 may set different reference points, so energies cannot be compared.

III. GROUND-STATE SPECTRUM OF NEUTRAL POLYAMPHOLYTES

Following the reasoning given in Sec. I and empirical observations, we expect the ground state of neutral PAs to be compact. It would be natural to consider an extensive form of the energy of the ground state with a surface correction. Phenomenologically, this can described as

$$\overline{E}=A_1 q_0^2 N+A_2 q_0^2\sqrt{N}, \tag{5}$$

where the overbar represents an average over quenches. The second term in Eq. (5) represents the 2D surface correction. Unlike short-range interacting systems, it is not obvious that

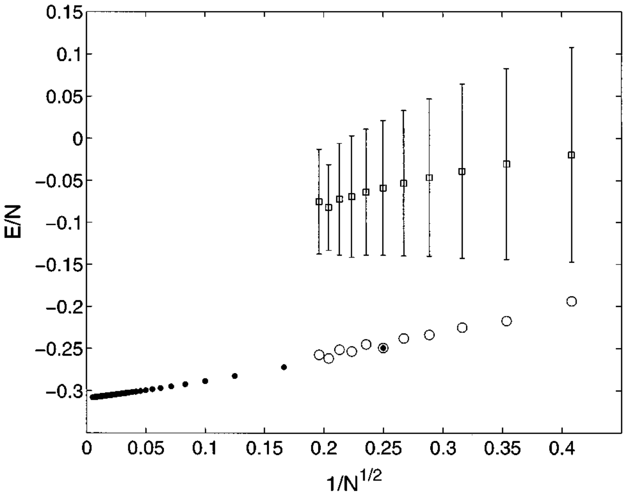

FIG. 1. Ground-state energies per monomer [28] for neutral sequences of lengths 6–26 monomers. For each length, boxes represent the mean value over all quenches studied, while error bars represent the standard deviation. The results for the alternating sign quench are represented by open circles. The energy of a salt-crystal plane is represented by dots.

the 2D Coulomb interaction produces such a form of $\overline{E}$. For instance, the energy of a *randomly* selected spatial configuration of a neutral sequence is expected to be of order $N\ln N$, i.e., it grows faster than N.

A convenient comparison point for the ground-state energies is provided by a checkerboard configuration (''salt crystal'') of charges, which is the ground state of a 2D Coulomb gas on a lattice [21]. It can be shown that for such an arrangement of charges the energy is extensive. Dots in Fig. 1 depict the energy per monomer for finite salt-crystal configurations forming a square consisting of $N=4n^2$ ($n=2,3,4,\dots$) charges. The energy of such a crystal is given by

$$E=-0.31q_0^2N+0.26q_0^2\sqrt{N}. \tag{6}$$

Not surprisingly, in PAs the ground state of quenches that are an alternating sequence of positive and negative charges (open circles in Fig. 1) follow the same law. However, a typical quench cannot assume a salt-crystal-like ground state. Results of evaluating all ground-state energies for the different quenches are depicted in Fig. 1. For each length, we display the mean and standard deviation of the ground-state energy taken over the different quenches. The mean energies may be fitted to an extensive form

$$\overline{E}=(-0.133\pm0.005)q_0^2N+(0.30\pm0.02)q_0^2\sqrt{N}. \tag{7}$$

Results must be considered with caution due to the rather short chains studied. A definite exclusion of possible logarithmic corrections would require the consideration of chain lengths larger by at least one order of magnitude. Nevertheless, since the energy of a salt crystal bounds from below the ground-state energies, we believe that the extensive form is valid.

The distribution of the ground-state energies per monomer, for the ensemble of quenches, is relatively broad even for the largest N's considered: Fig. 2 depicts the distribution of the ground-state energies of $N=16$ and 18 (all possible quenches) and 20 monomers (a partial sample only). Nevertheless, the standard deviation σ of the energy per monomer gradually decreases with increasing N. In systems with short-range interactions the energy of a large random system may deviate from the ensemble-averaged mean by an amount $\sim\sqrt{N}$. This is usually a consequence of the fact that the total energy of the system is (approximately) a sum of the energies of the subsystems: For example, the total energy is a sum of energies obtained by dividing the system into two halves. This property is referred to as self-averaging. Figure 3 demonstrates the linear dependence of the standard deviation of the energy per monomer σ on $1/\sqrt{N}$, which means that the fluctuations of the total energy are $\sim\sqrt{N}$. If the linear dependence may be extrapolated to longer chains (re-

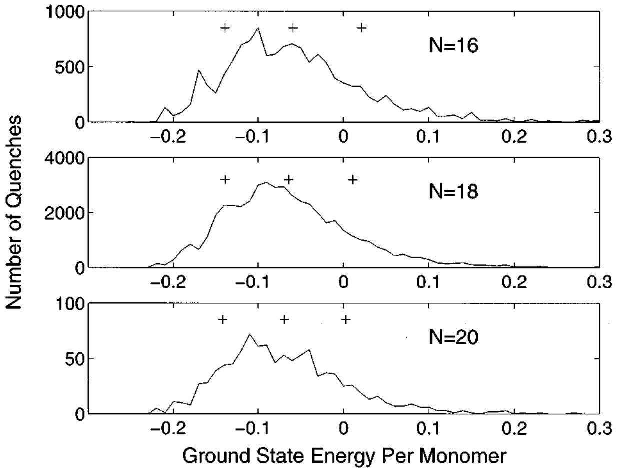

FIG. 2. Histogram of the ground-state energy per monomer [28] for all quenches of lengths 16 and 18 monomers and a partial sample of quenches of length 20 monomers. Crosses indicate mean and standard deviation limits. The bin size is $0.01q_0^2$.

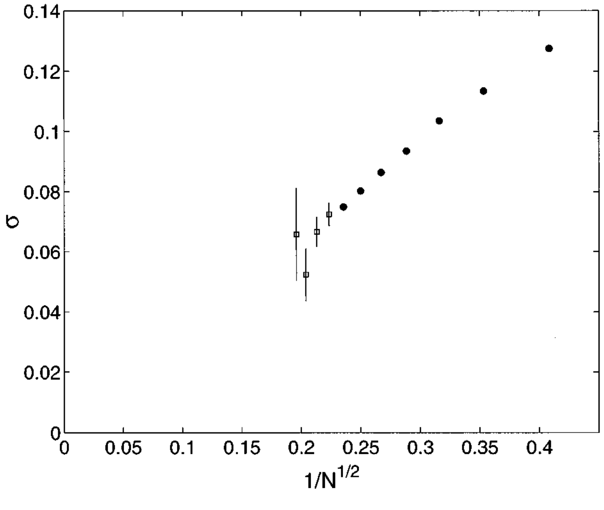

FIG. 3. Standard deviation of the ground-state energy per monomer σ [28], as a function of $1/\sqrt{N}$, for neutral quenches of lengths $6,8,\dots,26$ monomers. Error bars denote 98% confidence levels when the standard deviation was estimated for partial samples, in the four leftmost cases.

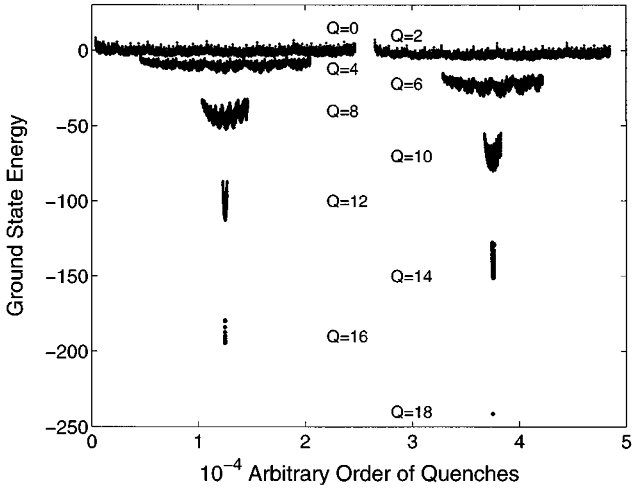

FIG. 4. Ground-state energies for all quenches of length 18 monomers [28]. The abscissa depicts an arbitrary order of quenches. Annotations denote the excess charge of the bands the energies group into.

garded with caution due to the short lengths investigated here) we may conclude that our system is self-averaging. However, if we split a large 2D *neutral* PA into two equal parts, usually neither of the halves will be neutral. On the contrary, typically each half will be charged by an equal and opposite charge $Q' \sim \sqrt{N}$ and thus have electrostatic energy of order $-Q'^2 \ln R' \sim -N \ln N$. Moreover, as will be shown in the next section, such charged subchains will be expanded, i.e., the spatial conformations of the subchains will not resemble the configuration of the entire PA. Nevertheless, we may use a slightly modified concept: In a very long neutral PA, one can usually find several special points such that splitting the PA at those points will divide it into several large *neutral* subsystems (see, e.g., Ref. [22]). The total energy of a PA can now be regarded as the sum of the energies of these separate segments.

IV. EXCESS CHARGE EFFECTS

The nonvanishing excess charge Q has a profound effect on the energies and spatial conformations of PAs. Figure 4 depicts the ground-state energies of all quenches of PAs of $N=18$. Every point in this figure corresponds to a different quench. The ground-state energies split into bands, each of which corresponds to a different Q. The distance between the band of neutral quenches and the rest of the bands increases approximately as Q^2 due to the appearance of a long-range electrostatic term $-Q^2 \ln R$, where the length R characterizes the spatial extent of the PA in the ground state. (The length R depends on Q; however, $\ln R$ has a minor effect on the leading Q^2 dependence.) One should keep in mind that, in general, the absolute values of the energy difference between the bands depends on the choice of the reference point r_0 in Eq. (4). We note that bands remain relatively narrow, i.e., the ground-state energy weakly depends on the details of the specific quench. Only when Q approaches $q_0 N$ the bands broaden, i.e., the details of the quench have a more significant influence on the overall energy.

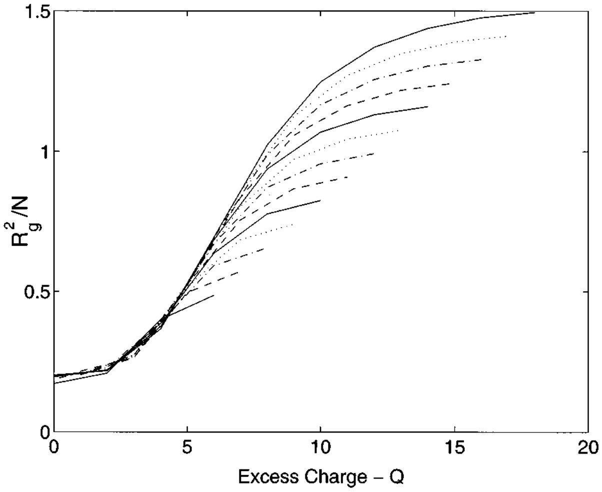

FIG. 5. R_g^2/N vs Q [28]. Curves represent different lengths ($N=6, 7, \ldots, 17, 18$ from bottom to top). Note the collapse of the curves at low Q and the gradual deviation as Q is increased.

The excess charge is an important parameter determining the shape of the ground state as well. Specifically, it determines whether the ground state is compact or expanded. We measure the typical size of a configuration by its root-mean-square size called the radius of gyration R_g. A compact shape is defined by $R_g \sim N^{1/d}$. In two dimensions this means that R_g^2/N is independent of N. In Fig. 5 we plot R_g^2/N as a function of Q for the different values of N. Each point is an average over all possible quenches of the specific N and Q. The most striking feature of Fig. 5 is that for small Q all the curves, for different values of N, collapse onto the same curve. Thus, even for very large N a minute charge Q can significantly increase R_g. This means that among the ensemble of random quenches in the $N \to \infty$ limit a vanishing portion remains compact. Even if the ensemble is biased towards neutrality, i.e., $Q_{\mathrm{typical}} \sim N^x$, where $1 \gg x > 0$, the resulting configurations will be expanded. Only exceptional quenches, where the excess charge is very small even for large N, will remain compact. This result may also be incorporated within the charged drop model for a PA. In two dimensions $Q_R \sim N^{1/4}$, but the logarithmic potential creates a certain difference with respect to higher dimensions: Because the potential has no finite asymptotic value, the charged drop will always find it favorable to disintegrate into distant droplets with an infinite energy gain. Hence, in a continuum model $Q_c = 0$ and we except an expansion in the size of the ground state of the PA for any excess charge. This is very different from 3D systems [17,18], where $Q_c \propto Q_R \sim \sqrt{N}$ so a finite portion of all random quenches remains compact. Once the critical charge is exceeded, the ground state will begin expanding, but does not immediately become fully stretched. Numerical results show that in two dimensions for $Q \sim N^{0.7}$ the resulting configuration is completely stretched, i.e., $R_g \sim N$. This implies that if the charge is a finite fraction of the size, i.e., $Q \sim N$, the ground state is fully stretched.

V. ANNEALED ENSEMBLE

Thus far we have considered quenched sequences in which charges are fixed in position along the chain. We now

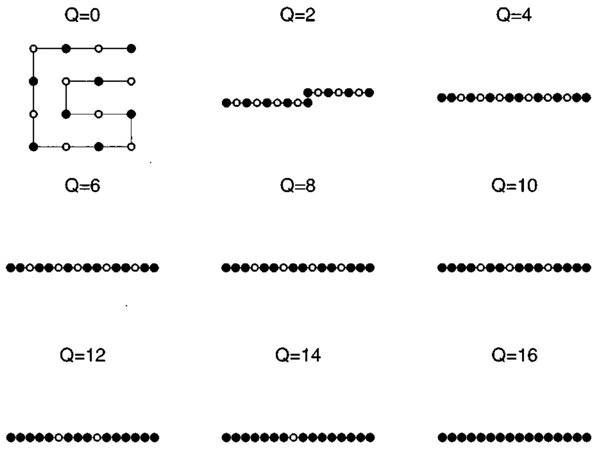

FIG. 6. Ground-state configuration for annealed sequences of length 16, with an overall excess charge restriction Q. Opposite charge types are denoted by open and full circles.

remove this restriction, allowing charges to exchange positions along the chain, maintaining the overall excess charge and number. (Two charges cannot be located at the same site, thus creating a double or vanishing charge.) We shall refer to this as an *annealed* ensemble of PAs. The ground-state configurations for the ensembles of $N=16$ and different values of Q are shown in Fig. 6.

For the neutral ensemble ($Q=0$) the ground state is naturally a sequence of charges alternating in sign that form a salt-crystal configuration, in the same way that free charges form such a crystal [21]. This spatial arrangement of the charges can be obtained by many different spatial configurations of the chain, making the ground state highly degenerate. For any nonzero excess charge we observe a sharp transition and the ground state has a fully stretched rodlike shape. For the sizes considered here, the ground-state configuration and charge sequences were unique.

Previously, we have seen that for a finite Q, the ground-state configuration of the quenched ensemble expands. In the annealed case the expansion is much more abrupt: The PA is completely stretched for any minute Q. It was suggested [17] that an annealed PA in three dimensions, with a large enough excess charge, might find it favorable to expel the excess charge in the form of highly charged fingers, while most of the monomers remain in a globule. In two dimensions the behavior seems to be quite different: A small excess charge suffices to stretch the PA into a straight line. The positions of the charges on that line are determined as follows: In general, the charges attempt to maintain an alternating sequence; this is not strictly possible because of nonvanishing Q. The excess charge is spread out almost uniformly (up to logarithmic corrections) along the PA.

These results should be regarded with caution. Contrary to the quenched ensemble, where the ground state is averaged over many quenches, thus smoothing out lattice effects, the ground state of the annealed ensemble corresponds to a single configuration of a single sequence. The chains studied might not be long enough to overcome this problem.

VI. DISCUSSION

We have studied the ground-state properties of a model 2D PA. We found that neutral quenches have a compact, dense ground state, whose energy can be described as an extensive energy term with a surface correction. The ground-state energies of the different quenches may be described by energy bands, each band corresponding to a certain excess charge. The specific sequence of charges is of a small influence, creating small fluctuations about the mean within the bands (for neutral quenches the ground-state energy is even self-averaging over all possible quenches). When the charge sequence is annealed (not quenched) the shape of the ground state is much more sensitive to excess charge, i.e., the PA is fully stretched for any $Q\neq 0$. The results are different from those obtained for a similar 3D model [18]. The nature of the 2D Coulomb interaction accounts for this difference. Both cases, however, match the expectations derived from an analogy with a charged drop. The main drawback of the method we applied throughout this study is the limited size of the systems we can fully investigate. Although we surpassed the maximal length studied in three dimensions, some results may be suspected as arising from finite-size and lattice effects. A major increase in computer capabilities is required to carry this method to larger systems.

Several authors [13,23] suggested that, at low temperatures, a PA may undergo a freezing transition, as do some models of polymers with a short-range interaction [5,24,25] and other disordered systems. Should this be the case, then the ground-state properties do not provide a full description of the zero-temperature behavior of the system. Our investigation of such a transition was not conclusive, but indicates its absence, at least in the sense that the requirements of the random energy model [26] are violated. This is in agreement with predictions of Pande *et al.* [27] that long-range interacting systems would not undergo a glass transition.

ACKNOWLEDGMENTS

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