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Charged polymers in high dimensions

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A Monte Carlo study of charged polymers with either homogeneously distributed frozen charges or with mobile charges has been performed in four and five space dimensions. The results are consistent with the renormalization-group predictions and contradict the predictions of Flory-type theory. Introduction of charge mobility does not modify the behavior of the polymers.

Linear polyelectrolytes[1,2] behave very differently from neutral polymers, since their monomers interact with each other via long-range electrostatic repulsive potential. In most practical cases, this repulsive interaction is screened by counterions present in the solvent. Although no exact treatment of the general problem is available, many qualitative and quantitative features are well understood (see, e.g., Ref. 3). When the counterion concentration is low, the screening effects can be neglected, which considerably simplifies the problem. More than a decade ago, two solutions were suggested in the case of unscreened interaction: a Flory-type (FT) approach[4] and a renormalization-group (RG) approach.[5] The extensions of Flory theory[6] are known to give excellent predictions in many cases (see, e.g., Ref. 7). The case of electrolytes is an exception: there are significant differences between the predictions of FT and RG. In particular, the theories predict very different values of the exponent ν, which characterizes the power-law dependence of the radius of gyration (rms size) R_g of the polyelectrolyte on its internal length (number of monomers) L: $R_g \sim L^{\nu}$.

In this work, a Monte Carlo (MC) study of polymers embedded in d dimensions ($d=4$ and 5) with repulsive interactions that fall off as $1/r^{d-2}$ has been performed. Two different cases have been considered: a case of uniformly charged polymer chain ("frozen charges"), and a case in which discrete charges can move along the chain ("conducting polymer"), while their positions are determined by the statistical mechanics of the problem. The obtained results are compared with FT and RG predictions. The results for the frozen-charges case are in excellent agreement with the RG predictions, and exclude the predictions of FT. Surprisingly, it is found that the case of conducting polymer essentially coincides with the case of frozen charges, i.e., both cases are described by the same critical exponent ν, and the charge fluctuations along the chain are small.

Spatial configurations of a polymer can be described by the positions of its monomers $\mathbf{r}(x)$, where x is the internal label of the position of a monomer along the chain, while $\mathbf{r}$ is the actual position of the monomer in a d-dimensional space. This geometrical description must be supplemented by the distribution of the charge density (divided by $\sqrt{k_BT}$) $\sigma(x)$ along the chain. In the continuum limit the statistical mechanics of such a chain is described by the Hamiltonian

$$\frac{\mathcal{H}}{k_BT}=\frac{K}{2}\int_0^L dx\left(\frac{d\mathbf{r}}{dx}\right)^2+\frac{1}{2}\int_0^L\int_0^L dx\,dx'\frac{\sigma(x)\sigma(x')}{|\mathbf{r}(x)-\mathbf{r}(x')|^{d-2}},$$

where K is the entropic force constant, while the second term represents the electrostatic repulsion. If the charges are immobile and homogeneously distributed then $\sigma(x)=\sigma_0$. The partition function of the polymer is obtained by the functional integration of $\exp(-\mathcal{H}/k_BT)$ over all positions $\mathbf{r}(x)$ of the monomers. In the case of a conducting polymer, an additional integration over $\sigma(x)$ must be performed, subject to the restriction of the total charge to a constant.

de Gennes *et al.*[4] devised a Flory-type theory which derives the overall size R_g of a polymer by equating the entropic and electrostatic parts of the free energy. They obtained a value of $\nu=\nu_F\equiv 3/d$, which is supposed to be valid for $3\le d\le 6$. (From a simple dimensional analysis one can see that the *long-range* electrostatic repulsion is irrelevant for $d>d_u=6$.) At the same time it has been noted by Pfeuty, Velasco, and de Gennes[5] that the repulsive term in $\mathcal{H}$ under rescaling generates an additional term, which corresponds to *short-range* repulsive (self-avoiding) interaction. The latter interaction is irrelevant for $d>4$. Other terms of $\mathcal{H}$ do not contribute anything to the rescaling of the *long-range* repulsive term. Therefore, for $4=d_l\le d\le d_u$, one needs to consider only the electrostatic interactions, and to *all orders* in a (d_u-d) expansion one finds[5] $\nu=\nu_{\rm RG}\equiv 2/(d-2)$. (Note that $\nu_{\rm RG}=1$ for $d=d_l$.) For $d<d_l$, the polymer is essentially stretched, and can be characterized[8] by its transverse fluctuations h, which scale with its linear dimension as $(\langle h^2\rangle)^{1/2}\sim L^{\zeta}$. It has been found[8] that $\zeta=d/2-1$ for $2\le d\le 4$, and $\zeta=0$, for $d<2$. Moreover, for $d\le 3$ the electrostatic energy increases faster than the linear size of the polymer, and its integrity can be maintained only by unbreakable bonding potentials.

The differences in the values of ν between the predictions of FT and RG are very significant for $d>3$. Although in the practical case of $d=3$ both theories would predict $\nu=1$, FT claims that this is a marginal dimensionality, and the polymer can be expected to be extremely crumpled, while according to the RG approach the three-dimensional polymer is well below its d_l, and is expected to be asymptotically straight with mild transverse fluctuations[8] ($\zeta=\frac{1}{2}$). It is impossible to compare FT and RG directly, since FT represents an uncontrolled approximation, while RG provides a prediction for ν, which is an asymptotic expansion to all orders in d_u-d. While it is reasonable to accept the prediction of RG as the true answer, it is useful to compare the predictions of both theories with the results of MC simulations.

In the case of a conducting polymer, the problem cannot be solved exactly. However, it has been speculated[8] that in this case all charges will migrate to the boundary of the object of size R_g, leading to electrostatic repulsive energy proportional to L^2/R_g^{d-2}, and the expansion of a chain due to those interactions will be balanced by the elastic (entropic) attraction (R_g^2/L). Balancing these two energies one recovers the Flory result $R_g \sim L^{\nu_F}$, although the system is no longer self-similar since the boundaries play a special role.

The model of a charged polymer considered in this work is a linear chain consisting of L atoms ($3 \le L \le 129$) embedded in d-dimensional discrete space (hypercubic lattice). I considered $d=4$ and 5, where the differences between the various theories are strongly pronounced. The atoms can be positioned at the vertices of the lattice, and the distance between the neighboring atoms of the chain can vary between zero and four, without any energetic cost. Such nearest-neighbor "square-well" potential has been previously used in continuum MC simulations of tethered surfaces[9] and in the simulations of linear polymers on lattices.[10] The repulsive electrostatic interaction $\mathcal{U}=\sum_{(i,j)}U(|\mathbf{r}_i-\mathbf{r}_j|)$ has been implemented by assigning energy $U(r)$ to every pair of charges at distance r from each other, where $U(r)/(k_BT)=c'/(c+r^2)^{(d-2)/2}$, with $c=c'=4$. Presence of the constant c in the denominator "regularizes" the repulsive energies at $r=0$, while c' in the numerator represents the squared value of an elementary charge. Typical interaction energies between the nearest neighbors are therefore somewhere between 0.1 and 1 k_BT. The choice of c' is quite important: If the prefactor of the interaction is too large (small) one will see a gradual crossover from $\nu=1$ ($\nu=\frac{1}{2}$) to the asymptotic value of ν. The total number of charges has been chosen to be equal to the number of atoms. The problem, therefore, does not address the question of short length-scale behavior of a weakly charged polymer.

An elementary MC move consists of a random choice of an atom and an attempt to move it by one lattice constant along one of the d perpendicular axes. The move is accepted if the resulting configuration has a lower energy than the original one. Otherwise, the move is accepted with the probability $\exp[(\mathcal{U}_{\text{init}}-\mathcal{U}_{\text{fin}})/k_BT]$. During one MC time step, on the average, one attempt is made to move every atom. In the case of a conducting polymer, in addition to the motion of the atoms, charges may migrate from one atom the neighboring one, in accordance with the same probabilistic rule as the motion of the atoms, and in a single MC time step an attempt is made to move every charge. Several charges, therefore, have a finite probability to accumulate on the same atom.

The relaxation time τ (the time between two statistically independent configurations) is approximately equal to the time it takes the chain to diffuse its own radius of gyration,[11] i.e., it is expected to increase as LR_g^2. If the distances are measured in lattice constants and the time is measured in MC time steps, then $\tau \approx LR_g^2$. The actual length of each MC run was $t=10^4L$, and, therefore, the statistical accuracy decreased with increasing L: For small L's the simulation time exceeded τ by 4 orders of magnitude, while for the largest L, $t\approx\tau$. Accordingly, the accuracy of the measured R_g was better than 1% for small L, and as bad as 30% for $L=129$. The actual accuracy was established by comparing the results of several runs (for small L), or by comparing partial averages (for large L). These results are consistent with the data scatter as seen in Fig. 1. The total execution time for $L=129$ was 12 and 6 days of CPU time on the Sun4 minicomputer for the conducting polymer and frozen-charges cases, respectively.

For polymers with immobile charges, the MC results confirm the predictions of RG: Crosses in Fig. 1 depict the dependence of R_g on L. The logarithmic plot in Fig.

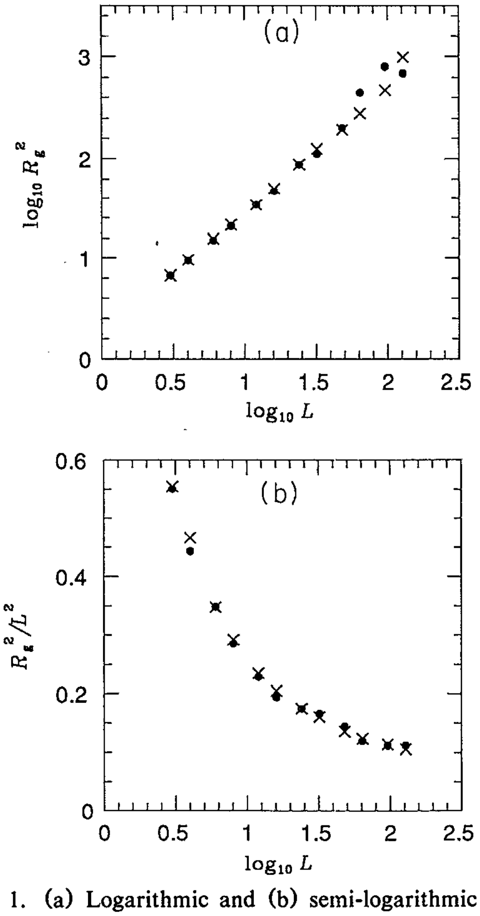

FIG. 1. (a) Logarithmic and (b) semi-logarithmic plots of the radius of gyration R_g of a polymer as a function its linear size L in (a) $d=5$ and (b) $d=4$ dimensions. Solid circles and crosses represent the cases of mobile charges and frozen charges, respectively.

1(a) represents the $d = 5$ case. From a fitted slope of the graph, I find $\nu = 0.67 \pm 0.03$, which agrees quite well with $\nu_{\mathrm{RG}} = \frac{2}{3}$, and excludes the value of $\nu_F = \frac{3}{5}$. In $d = 4$, an extremely slow crossover is observed: On a regular logarithmic plot, the slope of the graph gradually increases and can be extrapolated to $\nu = 0.98 \pm 0.05$, where the error limits represent a subjective estimate of the accuracy of the extrapolation. Slowness of the crossover is magnified in the semilogarithmic representation of Fig. 1(b): R_g^2/L^2 is supposed to approach a constant, as $L \rightarrow \infty$. To summarize the $d = 4$ case: The obtained result is consistent with $\nu_{\mathrm{RG}} = 1$ and contradicts $\nu_F = \frac{3}{4}$.

The results obtained for polymers with mobile charges are somewhat surprising. It is obvious from Fig. 1, where the conducting polymer results are represented by solid circles, that they behave essentially identically with the polymers with frozen charges. A closer examination of the charge distribution along the chains, shows that despite the mobility of charges, large fluctuations of charge density are completely absent. The result is inconsistent with the earlier predictions.[8] Nevertheless, it can be qualitatively understood: One should notice that for $\nu = \nu_{\mathrm{RG}}$, the total electrostatic repulsion energy of a polymer is independent of L (as opposed to the case of $\nu = \nu_F$, where this energy grows as $L^{6/d-1}$). Thus the energy gain as a result of charge redistribution in a conducting polymer is *independent* of L. At sufficiently large temperature there should be no charge redistribution, while at lower temperatures some redistribution will appear, up to a point where the entropic cost will prevent further charge concentration in few selected regions. Since the charge redistribution causes only a finite (L-independent) change in the energy, it is, therefore, plausible to assume that the chain with mobile charges will behave similarly to the homogeneously charged polymer.

Results obtained in this work confirm the validity of the RG approach and exclude the predictions of Flory-type theory. Further work needs to be done to gain more theoretical understanding of the conducting polymer case. The results also imply that the $d = 3$ case is deeply in the asymptotically flat regime, and the primary interest there should concentrate on the scaling of the transverse fluctuations. However, one should beware of slow crossovers even in the three-dimensional case.

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