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Polyelectrolyte configuration in a disordered medium

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We consider the configuration of a linear polyion embedded in a disordered medium with quenched fluctuations in the density of ionic sites that comprise the disorder. Expressions for the disorder-averaged interactions among the polyion beads are derived. The problem of polyion structure in a quenched disordered medium is thus reduced to that of a self-interacting polymer with adjusted pair potentials among its units. This class of problems is solvable by existing theories for polymer and polyelectrolyte configuration. We analyze the problem using the Feynman-Bogoliubov variational method with a Gaussian reference Hamiltonian and compare the results of this approach with those of Monte Carlo simulations performed using the same disorder-averaged pair potentials. At all conditions, the charged disorder leads to a contraction of the polymer, the effect being strongly dependent on the quenching temperature and the concomitant permittivity of the disorder which effectively determine the magnitude of the potential fluctuations in the system. At high disorder strength, the scaling characteristic of a self-avoiding chain is retained for shorter polyions. For sufficiently long polymers, however, the size of the polymer coil becomes almost independent of the degree of polymerization N. The transition between the two regimes takes place at the degree of polymerization at which the characteristic distance among the beads, measured in terms of the radius of gyration R_g, reaches the distance $r_{\min}$ corresponding to the minimum of the effective disorder-averaged pair potential among the beads.

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I. INTRODUCTION

The configuration of an ionized macromolecule in solution or in a porous material is strongly affected by the long-ranged Coulombic interactions among the charged groups on the polymer chain. The electrostatic repulsions enhance steric exclusion effects, thus leading to the swelling of the polyion coil [1–5]. Additional effects such as the rigidity of bonds and interactions with molecules of the solvent and other components in the system may also contribute to the equilibrium conformation of the polyion. In view of their importance in engineering and biophysics, polyelectrolyte solutions have long been the subject of intense experimental and theoretical research [1–4,6]. Many features of the behavior of polyelectrolyte solutions have been dealt with in theoretical treatments ranging from classical mean-field theories to integral equation approaches [5,7–29] and simulations [28–38]. It is fair to say that the structural behavior of simple polyelectrolyte solutions is reasonably well understood. Technological processes and biological systems, however, often involve polyelectrolyte molecules at interfaces or in porous materials characterized by various degrees of disorder in the composition and spatial distribution of steric obstacles or polar groups which may interact with the units of the polyion. The effects of disordered media on neutral polymers have been addressed in the literature and interesting localization behavior resulting in the overall contraction of the coil has been unanimously predicted [39–49]. The case of the chain with long-ranged intramolecular forces in a hard-core disordered medium has also been studied [43]. In the present paper, these considerations are extended to ionic macromolecules interacting with random media that are comprised of nonuniform charge distributions with quenched spatial fluctuations. Specifically, we will assume that the quenched disordered medium may contain uncorrelated fixed obstacles and ionic sites frozen at a configuration that corresponds to an equilibrium distribution at some higher temperature, T', at which the disordered material has been prepared. An example of the above kind of charged disordered matrix is [50,51] a macroporous, water-filled network with randomly located cationic and anionic headgroups. While neutral as a whole, the matrix is characterized by quenched spatial fluctuations in the charge density due to the random distribution of fixed ionic sites [50,51]. We will assume that the density distribution of these sites can be approximated by the Debye-Hückel form [52,53] for spatial correlations at the prequenching temperature T' at which the disorder has been equilibrated before quenching takes place. This fixed configuration of the disorder particles persists during the time of observation of the system at an ambient temperature $T < T'$. A macromolecule absorbed in this porous material, however, undergoes thermal motion. It assumes various configurations and visits many different disordered environments. The average configuration of the macromolecule in the matrix depends on both the intramolecular forces and on the interactions with the disordered material. In this study, we aim to estimate the effect of interactions with the disordered medium on the conformation of the chain. The model system we will consider in our analysis will be described in terms of an Edwards Hamiltonian [54] for a self-avoiding macromolecule supplemented by the Coulombic interactions among the charged polyion units [8,10–17,22–27] and by the forces between the units of the polymer and the fixed sites of the disordered medium. In previous studies of polymers in disordered media, the disordered material was usually modeled as "a medium in which a certain number of obstacles is frozen at random locations" [43]. In the present study, the medium can comprise both steric obstacles and fixed ionic sites interacting with the polyion through the long-ranged Coulombic potential. While our analysis applies to both types of the disorder, we mainly focus on the effects of charged disorder on the structure of the polyion. In order to carry out the disorder average, we treat the quenched disorder as an annealed disorder in the adiabatic limit, a procedure allowed [44,45,47,50] at the specific conditions considered in the present study. In general, the treatment of quenched and annealed disorders must be carried out differently. In the former case one needs to average the free energy while in the latter the disorder-averaged partition function is calculated. In sufficiently large, self-averaging systems, however, the two types of disorder can be treated in an analogous manner [42,44,45,47,55–59]. As noted in these and other contexts previously, this is so because under these circumstances, the disordered medium can be represented as an ensemble of several large subsystems, each of which is larger than any relevant length scale of the problem of interest. During a macroscopic time of observation, the macromolecule undergoing thermal motion through the medium will visit a representative ensemble of subsystems with different configurations of the disorder. This way, the macromolecule will sample the disordered environments with the probability that is arbitrarily close to that characteristic of the annealed case in the adiabatic limit. The quenched and the adiabatic annealed averages are therefore equivalent in the limit of large, self-averaging systems. The argument pertains to the calculation of polymer properties averaged over all initial positions in the sample. It does not apply to the cases of a grafted macromolecule or of a chain trapped in a medium of obstacles whose concentration exceeds the percolation threshold [47]. The analysis based on the equivalence between the two averages is suitable for situations where the polymers are sufficiently mobile to retain the self-averaging properties described in the above argument. As discussed in several studies [44,45,47,50,59], the use of this equivalence avoids some of the algebraic complexity associated with carrying out a replica analysis [40,42,43] without altering any of the structural results that pertain to the statistical properties of the fluid in a medium with prescribed disorder-disorder correlations. In the present context, we employ this approach to derive expressions for the disorder-averaged Hamiltonian of the polyion that are analogous to the solvent-averaged McMillan-Mayer potentials usual in standard treatments of mixtures and solutions [52,53]. The polyion configuration can then be obtained by any method selected from a variety of approximate theories applicable to simple polyelectrolyte solutions. The particular procedure that we shall use is the variational path integral approach which has been used in various forms in a number of recent articles [16,19,22–26]. The disorder-averaged Hamiltonian that we obtain can, however, be treated by other analytical approaches as well as simulations. In the present work, predictions of the variational method in a number of characteristic situations will be compared with the results of Monte Carlo simulations performed using the disorder-averaged Hamiltonian of the polyion.

The paper is organized as follows. In Sec. II, the model Hamiltonian is specified and the averaging procedure leading to the expressions for the disorder-induced interactions is described. In Sec. III, we consider the application of the variational method of Ref. [16] to a system characterized by the above disorder-averaged Hamiltonian. In Sec. IV, the details of the Monte Carlo simulations carried out on the same model are given. Finally, in Sec. V, numerical results and predictions of the model are discussed. A comparison between the results of the variational approach and the simulation is presented. Some limitations of the present analysis are pointed out and planned improvements are briefly outlined.

II. ANALYSIS

A. General considerations

The polyion embedded in the disordered medium is modeled as a necklace of N equal units or beads of excluded volume, u_2, each carrying a charge, q. The bonds among the neighboring beads are described as harmonic springs, the spring constant being equal to $3kT/2l^2$, where k is the Boltzmann constant, T the absolute temperature, and l the mean (Kuhn) segment length in the absence of anharmonic interactions. The beads located at positions $\{\mathbf{r}_m\}$ interact with each other through the excluded volume potential, approximated by the standard hard-core Hamiltonian H_{hc}.

$$H_{\text{hc}}=\frac{u_2}{2}\sum_{m,m'}\delta(\mathbf{r}_m-\mathbf{r}_{m'})+\frac{u_3}{3!}\sum_{m,m',m''}\delta(\mathbf{r}_m-\mathbf{r}_{m'})\delta(\mathbf{r}_{m'}-\mathbf{r}_{m''})+\cdots \tag{1}$$

consisting of the two-body, three-body, and higher-order contributions. For the time being, we will be concerned solely with the two-body pair interactions

$$u_{mm'}=u_2\delta(\mathbf{r}_m-\mathbf{r}_{m'}) \tag{2}$$

which dominate the hard-core exclusion at moderate segment densities. In addition to the short-ranged steric effect, the ionized beads repel each other through the Coulombic potential u^e:

$$u^e_{mm'}(\mathbf{r}_m-\mathbf{r}_{m'})=\frac{\lambda}{|\mathbf{r}_m-\mathbf{r}_{m'}|}\ , \tag{3}$$

where $\lambda=q^2/4\pi\varepsilon kT$ and the thermal energy kT is used as the energy unit throughout the paper. In the presence of a simple electrolyte, the repulsions among the beads are electrostatically screened as discussed briefly in paragraph Sec. II B 3. The screening due to the polyelectrolyte counterions and interactions among distinct polyions will not be considered since infinite dilution of the polymer is assumed. A fraction of the counterions attracted to the polyion at these conditions may still be considered through Manning's limit of polyion charge density. According to this limit, the counterions will effectively shield the polyion charge in excess of the critical charge density [60] determined by the relation

$$q/l=4\pi\varepsilon kT/e_0 . \tag{4}$$

In addition to the intramolecular forces, the polymer beads also interact with the disorder. For the time being, we do not specify the form of the bead-disorder interactions except to restrict attention to two-body interactions. The Hamiltonian of a polyion can then be written as

$$H=\frac{3}{2l^2}\sum_m(\mathbf{r}_{m+1}-\mathbf{r}_m)^2+\frac{1}{2}\sum_m\sum_{m'}u_{mm'}(\mathbf{r}_m-\mathbf{r}_{m'}) + \sum_m\sum_d u_{md}(\mathbf{r}_m-\mathbf{r}_d) , \tag{5}$$

where the summation is over all polymer units m and disorder particles d, and pair potentials $u_{mm'}(\mathbf{r}_m-\mathbf{r}_{m'})$ and $u_{md}(\mathbf{r}_m-\mathbf{r}_d)$ comprise Coulombic, excluded volume, and other contributions to the bead-bead and the bead-disorder interactions, respectively. The instantaneous configuration of the polyion is determined by the coordinates of its units $\{\mathbf{r}_m\}$. The global structure of the polymer is, however, conventionally described in terms of the mean-square distances between pairs of beads

$$\langle|\mathbf{r}_m-\mathbf{r}_{m'}|^2\rangle=\left\langle\frac{\mathrm{Tr}|\mathbf{r}_m-\mathbf{r}_{m'}|^2 e^{-H(\{\mathbf{r}_m\},\{\mathbf{r}_d\})}}{\mathrm{Tr}\,e^{-H(\{\mathbf{r}_m\},\{\mathbf{r}_d\})}}\right\rangle_{\{\mathbf{r}_d\}} \tag{6}$$

where the set $\{\mathbf{r}_d\}$ represents the positions of the particles of the quenched disorder and the angular brackets denote the average over $\{\mathbf{r}_d\}$. Similarly, one obtains the thermodynamic properties from the free-energy function

$$\langle F\rangle=-\langle\ln\mathrm{Tr}\,e^{-H(\{\mathbf{r}_m\},\{\mathbf{r}_d\})}\rangle_{\{\mathbf{r}_d\}} . \tag{7}$$

In both Eqs. (6) and (7), the symbol Tr implies integration over the configurations of the polymer $\{\mathbf{r}_m\}$ at fixed configuration of the disorder, $\{\mathbf{r}_d\}$, and the angular brackets denote averaging over all realizations of the quenched disorder, $\{\mathbf{r}_d\}$. Quenched disorder averages are usually performed using the replica method. For quenched disorders, external to the observed macromolecule, however, the disorder can be treated as an annealed disorder in the adiabatic limit [44,45,47,50,55–59]. As noted in the aforementioned references and in the Introduction of the present work, treating a quenched disorder as an annealed one leads to identical statistical properties of the embedded polymer. Of course, we assume that the system is self-averaging in making this statement. The conclusions based on the simple physical interpretation outlined in the Introduction, as well as related thermodynamic arguments [44,47], have been reaffirmed by a perturbative renormalization-group analysis [45]. The reader is referred to these references for a thorough discussion of the subject. For the well-known case of the self-avoiding chain interacting with quenched steric obstacles below the percolation threshold [39,40,42–44,46–49], employing the equivalence between the quenched and the adiabatic annealed disorders is known to reproduce the structural results [43] of the replica analysis. The above equivalence has recently been exploited to study the effects of random media on macromolecular structure, penetrant diffusion, and quantum processes in liquids [44,45,47,50,55–59]. In view of this equivalence, we may reverse the sequence of the averaging operations in Eqs. (6) and (7) without affecting the statistical properties of the macromolecule. We begin our analysis by considering the average of the Boltzmann factor $e^{-H(\{\mathbf{r}_m\},\{\mathbf{r}_d\})}$ over the configurations of the disorder. It is convenient to assume a continuous spatial distribution of all disorder species s,

$$\rho_s(\mathbf{r})=\rho_s+\delta\rho_s(\mathbf{r}) , \tag{8}$$

where ρ_s is the average density of the disorder species, and $\delta\rho_s(\mathbf{r})$ its local-density fluctuation. The fluctuations around the mean are considered to obey Gaussian statistics; i.e.,

$$P[\delta\rho_s(\mathbf{r})]\sim\exp\left\{-\int\int\delta\rho_s(\mathbf{r})\chi_s^{-1}(\mathbf{r},\mathbf{r}')\delta\rho_s(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}'\right\} , \tag{9}$$

where $\chi_s^{-1}(\mathbf{r},\mathbf{r}')$ is the functional inverse of the density-density correlation function for species s,

$$\chi_s(\mathbf{r},\mathbf{r}')=\langle\delta\rho_s(\mathbf{r})\delta\rho_s(\mathbf{r}')\rangle=\rho_s\delta(\mathbf{r}-\mathbf{r}')+\rho_s^2h_s(\mathbf{r}-\mathbf{r}') , \tag{10}$$

and $h_s(\mathbf{r}-\mathbf{r}')=g_s(\mathbf{r}-\mathbf{r}')-1$ is the total correlation function of given species. Only the self-term $\rho_s\delta(\mathbf{r}-\mathbf{r}')$ will survive for an uncorrelated disorder characteristic of dilute steric obstacles. The charged disorder, quenched at certain temperature $T'>T$, is, however, assumed to retain the distribution characteristic of equilibrium at that temperature. This simply implies that we consider the disorder to have been in equilibrium at T' prior to quenching down to a lower temperature T. For the sake of analytic tractability, this distribution is approximated by the asymptotic low-density form [52,53]

$$h_s(\mathbf{r}-\mathbf{r}')=-\frac{\lambda'}{|\mathbf{r}-\mathbf{r}'|}e^{-\kappa'|\mathbf{r}-\mathbf{r}'|}$$

with

$$\lambda'=e_0^2/4\pi\varepsilon' kT' \tag{11}$$

and

$$\kappa'^2=4\pi\rho_e\lambda' .$$

Here, ρ_e denotes the number density of charged disorder sites, and the coupling constant $\lambda'(T')$ and the screening parameter $\kappa'(T')$ correspond to the quenching temperature T' and permittivity $\varepsilon'(T')$ that are different from the temperature of observation T and permittivity $\varepsilon(T)$ of our system. The sum over the disorder particles in the last term of the system Hamiltonian, Eq. (5), is now replaced by corresponding spatial integrals over the distributions, $\rho_s(\mathbf{r})$. The contribution to the effective Hamiltonian from the mean density, ρ_s [see Eq. (8)], is irrelevant since it represents a constant term independent of the configuration of the polymer. Therefore, although nonzero, it cannot affect the probabilities of different configurations of the chain. Moreover, in view of overall electroneutrality, this term vanishes for charged disorders. Only the terms corresponding to the density fluctuations are, therefore, retained in our analysis. Calculations for neutral polymers [39–48,55,59] show that these fluctuations induce an attraction among polymer units. As shown below, the same effect is observed for polyelectrolytes after the disorder average has been performed. Performing the functional integrals that correspond to the averaging over the density distributions of the disorder amounts to the calculation of an "influence functional," $\exp[I\{\mathbf{r}_m\}]$ [61]:

$$e^{I[\{\mathbf{r}_m\}]}=\left\langle \exp\left[-\sum_m\sum_s\int u_{ms}(\mathbf{r}_m-\mathbf{r}_s)\delta\rho(\mathbf{r}_s)d\mathbf{r}_s\right]\right\rangle_{P[\rho(\mathbf{r}_s)]}, \tag{12}$$

where the subscripts m and s correspond to a particular polymer unit and disorder species, respectively; the angular brackets denote the disorder average, and the probabilities P are given by Eq. (9). The above calculation is easily performed to yield:

$$e^{I[\{\mathbf{r}_m\}]}=\exp\left[\tfrac{1}{2}\sum_m\sum_{m'}\sum_s\sum_{s'}\int\int u_{ms}(\mathbf{r}_m-\mathbf{r}_s)\langle\delta\rho(\mathbf{r}_s)\delta\rho(\mathbf{r}_{s'})\rangle u_{m's'}(\mathbf{r}_{m'}-\mathbf{r}_{s'})d\mathbf{r}_s d\mathbf{r}_{s'}\right]. \tag{13}$$

This result applies to arbitrary types of disordered media provided the density fluctuations are adequately described by Gaussian statistics. Two types of disorder consisting of steric obstacles and charged sites will be considered in the following. No cross correlations between the two kinds of disorder particles will be assumed, so $\chi_{ss'}(\mathbf{r},\mathbf{r}')=\langle\delta\rho_s(\mathbf{r})\delta\rho_{s'}(\mathbf{r}')\rangle$ will be taken to vanish for $s\neq s'$. In view of this assumption and Eq. (13), the Hamiltonian H of Eq. (5) can be replaced by the disorder averaged form

$$\begin{aligned} H&=\frac{3}{2l^2}\sum_m(\mathbf{r}_{m+1}-\mathbf{r}_m)^2+\tfrac{1}{2}\sum_m\sum_{m'}\left\{u_{mm'}(\mathbf{r}_m-\mathbf{r}_{m'})-\sum_s\int\int u_{ms}(\mathbf{r}_m-\mathbf{r}_s)\chi_s(\mathbf{r}_s-\mathbf{r}'_s)u_{m's}(\mathbf{r}_{m'}-\mathbf{r}'_s)d\mathbf{r}_s d\mathbf{r}'_s\right\}\\ &=\frac{3}{2l^2}\sum_m(\mathbf{r}_{m+1}-\mathbf{r}_m)^2+\tfrac{1}{2}\sum_m\sum_{m'}\hat{u}_{mm'}(\mathbf{r}_m-\mathbf{r}_{m'}). \end{aligned} \tag{14}$$

According to the above result, the Hamiltonian can be expressed in terms of apparent pair potentials, $\hat{u}_{mm'}(\mathbf{r}_m-\mathbf{r}_{m'})$, which play the role of the disorder-averaged analog of the McMillan-Mayer pair potential between the beads m and m'. The effective potentials comprise the direct terms, $u_{mm'}(\mathbf{r}_m-\mathbf{r}_{m'})$, and the medium-induced attractions [43–48,62,63], corresponding to the third term of the right-hand side of Eq. (14). In the present case, this term is simplified by ignoring any correlations among different species of the disorder. Such correlations do not seem important in the present context but can, at any stage, be included in a straightforward manner.

Equation (14) can be analyzed by employing any of the various methods that have been developed to study configurational statistics of polymers with nonlocal bead-bead interactions. In order to illustrate the physical effects of the disorder on the structure of the polyion, we shall employ a variational path-integral method and the Monte Carlo simulation technique described in Secs. III and IV, respectively. Prior to doing so, however, we need to specify the nature of interactions between the beads and the disorder and to consider the expressions for the effective potentials $\hat{u}_{mm'}(\mathbf{r}_m-\mathbf{r}_{m'})$ pertaining to particular types of intramolecular and polymer-disorder interactions.

B. Specific examples

1. *Steric disorder*

We begin by briefly considering the well-known [39–49] example of a self-avoiding uncharged macromolecule in dilute steric disorder. In this case, the repulsive interactions between the polymer units are approximated by Eq. (2) and the same form with a different prefactor, u_d, describes the interaction between the polymer beads m and the disorder particles d. The disorder-averaged bead-bead potential $\hat{u}_{mm'}(\mathbf{r}_m-\mathbf{r}_{m'})$ introduced in Eq. (14) reads

$$\begin{aligned} \hat{u}_{mm'}(\mathbf{r}_m-\mathbf{r}_{m'})&=u_2(\mathbf{r}_m-\mathbf{r}_{m'})\\ &\quad-\int\int u_d\delta(\mathbf{r}_m-\mathbf{r}_d)\chi_d(\mathbf{r}_d-\mathbf{r}_{d'})\\ &\quad\times u_d\delta(\mathbf{r}_{m'}-\mathbf{r}_{d'})d\mathbf{r}_d d\mathbf{r}_{d'}\\ &=u_2\delta(\mathbf{r}_m-\mathbf{r}_{m'})-u_d^2\chi_d(\mathbf{r}_m-\mathbf{r}_{m'}). \end{aligned} \tag{15}$$

In the case of a medium of uncorrelated steric obstacles, which is the situation considered in many previous studies [39,40,42–44,59], the density-density correlation function can be written as [40,42,43]

$$\chi_d(\mathbf{r}-\mathbf{r}')=\rho_d\delta(\mathbf{r}-\mathbf{r}') \tag{16}$$

and Eq. (15) for $\hat{u}_{mm'}(\mathbf{r}_m-\mathbf{r}_{m'})$ becomes [43]

$$\begin{aligned}\hat{u}_{mm'}(\mathbf{r}_m-\mathbf{r}_{m'})&=[u_2-u_d^2\rho_d]\delta(\mathbf{r}_m-\mathbf{r}_{m'})\\&=u_2'\delta(\mathbf{r}_m-\mathbf{r}_{m'}) .\end{aligned} \tag{17}$$

Within the above approximation, the disorder-averaged bead-bead potential retains the form of the steric interaction among the self-avoiding beads but with a modified coupling constant $u_2'=[u_2-u_d^2\rho_d]$ replacing the excluded volume parameter u_2. This, of course, is a known result considered in earlier replica analyses [43] but has also been shown to be true via heuristic arguments [47] and Monte Carlo simulations [44]. It is interesting to note the independence of u_2' on the sign of the bead-disorder interaction [43]. Disorder particles attracting the polymer beads have the same overall effect as an equally strong repulsive disorder. The only difference is the change in the role of the sign of the density fluctuations. In the case of an attractive disorder, the polymer beads are being attracted to regions with higher density whereas they are trapped in regions of low density in the case of repulsive bead-disorder interactions. The presence of quenched disorder has an apparent effect on the "quality" of the solvent as reflected in the value of the coefficient u_2'. This is best illustrated in the case of the disorder particles with the excluded volume equal to the volume of the beads, $u_d=u_2$. Considering that the product $u_d\rho_d$ equals the volume fraction of the disorder obstacles ϕ_d, the effective coupling constant u_2' can be expressed by the relation

$$u_2'=u_2[1-\phi_d] . \tag{18}$$

A somewhat more complicated situation is obtained if u_d differs from u_2. In this case,

$$u_2'=u_2\left[1-\frac{u_d}{u_2}\phi_d\right] \tag{19}$$

can assume negative values leading to an effective attraction between the beads. These effects have, of course, been thoroughly studied by a number of alternative approaches [39–48,55]. We have briefly considered this case merely as an illustration of the application of the results of the preceding section. We note that the presence of another type of the disorder would not alter the expression for the disorder-induced excluded-volume contribution as long as different disorder species are not correlated.

2. *Ionized macromolecule in charged disorder*

We now turn attention to the more interesting and hitherto unexplored case of a self-avoiding macromolecule comprised of charged units interacting among themselves as well as with charged disorder particles through bare Coulombic potentials, Eq. (3). This system is related to, but different from the case of the polymer with long-ranged intermolecular forces in a purely steric disorder considered in Ref. [43]. The emphasis of the present work is on the effects of long-ranged polymer-disorder interactions. The disordered medium consists of charged sites of total density ρ_e, each carrying an elementary charge e_0 or $-e_0$. The quenched charge-density distribution is subject to Gaussian spatial fluctuations around neutrality, with the density-density correlation function, χ_e, described [52] by the Debye-Hückel form

$$\chi_e(\mathbf{r}-\mathbf{r}')=\rho_e\delta(\mathbf{r}-\mathbf{r}')-\frac{\rho_e\kappa'^2}{4\pi|\mathbf{r}-\mathbf{r}'|}e^{-\kappa'|\mathbf{r}-\mathbf{r}'|} , \tag{20}$$

where κ' corresponds to the temperature T' at which the disordered medium has been brought to equilibrium before the quenching took place, and which is higher than the current temperature T. According to Eq. (11), κ' also depends on the permittivity $\varepsilon'(T')$ that may differ from the current permittivity $\varepsilon(T)$ of the system at the conditions of observation. χ_e takes a particularly compact form in Fourier space where we have

$$\hat{\chi}_e(k)=\frac{\rho_e k^2}{k^2+\kappa'^2} . \tag{21}$$

The effective bead-bead potential obtained after integration over the density distributions of the charged disorder is

$$\hat{u}_{mm'}(\mathbf{r}_m-\mathbf{r}_{m'})=u_2'\delta(\mathbf{r}_m-\mathbf{r}_{m'})+\frac{\lambda}{|\mathbf{r}_m-\mathbf{r}_{m'}|}-\int\int\frac{\lambda}{|\mathbf{r}_m-\mathbf{r}_d|}\chi_e(\mathbf{r}_d-\mathbf{r}_d')\frac{\lambda}{|\mathbf{r}_{m'}-\mathbf{r}_d'|}d\mathbf{r}_d d\mathbf{r}_d' . \tag{22}$$

Replacing the real-space expressions for the bead-disorder interactions and the disorder-disorder density correlation function by corresponding Fourier transforms, and taking advantage of the convolution theorem, we can rewrite Eq. (22) as

$$\hat{u}_{mm'}(\mathbf{r}_m-\mathbf{r}_{m'})=\frac{1}{(2\pi)^3}\int\left\{u_2'+\frac{4\pi\lambda}{k^2}-\frac{4\pi\lambda}{k^2}\frac{\rho_e k^2}{k^2+\kappa'^2}\frac{4\pi\lambda}{k^2}\right\}e^{i\mathbf{k}\cdot(\mathbf{r}_m-\mathbf{r}_{m'})}d\mathbf{k} \tag{23}$$

or

$$\hat{u}_{mm'}(\mathbf{r}_m-\mathbf{r}_{m'})=u_2'\delta(\mathbf{r}_m-\mathbf{r}_{m'})+\frac{\lambda}{|\mathbf{r}_m-\mathbf{r}_{m'}|}-\frac{4\pi\lambda^2\rho_e}{\kappa'^2}\left[\frac{1}{|\mathbf{r}_m-\mathbf{r}_{m'}|}-\frac{1}{|\mathbf{r}_m-\mathbf{r}_{m'}|}e^{-\kappa'|\mathbf{r}_m-\mathbf{r}_{m'}|}\right] . \tag{24}$$

In writing Eq. (24), we assumed that the beads m and m' are monovalent and equally charged. In the case of arbitrary valences, z_m and $z_{m'}$, the Coulombic terms in Eq. (24) would be multiplied by the prefactor $z_m z_{m'}$. The first term in Eq. (24) corresponds to the excluded volume interaction between the beads, possibly modified by the effect of the disordered obstacles described by Eq. (17). The second term is due to the direct electrostatic interaction among the charged beads, and the last term describes the electrostatic screening of these interactions by the charged disorder. The screening power of the static charged disorder stems from the fact that the charged polymer beads prefer to reside in regions with charge density opposite to their own. According to Eq. (11), the screening parameter κ' of the disorder depends on the prequenching temperature (T') and the corresponding permittivity $\varepsilon'(T')$ at which the disorder has last been in thermodynamic equilibrium. In the interesting hypothetical case with T' equal to the actual temperature of the system T, and consequently, κ'^2 equal to $\kappa^2=4\pi\lambda\rho_e$, the screening term, estimated in Eq. (24), is equal to the screening effect of a simple electrolyte [52,53] whose ionic strength equals the ionic strength of the disorder. For real quenched systems, of course, $T'>T$, and the appropriate relation for κ'^2 is

$$\kappa_e'^2=4\pi\lambda\rho_e\frac{\varepsilon T}{\varepsilon' T'} . \tag{25}$$

For an arbitrary ion pair mm' with charges z_m and $z_{m'}$, Eq. (24) can then be rewritten as

$$\hat{u}_{mm'}(\mathbf{r}_m-\mathbf{r}_{m'})=u_2'\delta(\mathbf{r}_m-\mathbf{r}_{m'})+\frac{\lambda z_m z_{m'}}{|\mathbf{r}_m-\mathbf{r}_{m'}|}-\frac{\lambda z_m z_{m'}\varepsilon' T'}{\varepsilon T}\left[\frac{1}{|\mathbf{r}_m-\mathbf{r}_{m'}|}-\frac{1}{|\mathbf{r}_m-\mathbf{r}_{m'}|}e^{-\kappa'|\mathbf{r}_m-\mathbf{r}_{m'}|}\right] \tag{26}$$

or, in the limit of small $\kappa'|\mathbf{r}_m-\mathbf{r}_{m'}|$,

$$\hat{u}_{mm'}(\mathbf{r}_m-\mathbf{r}_{m'})=u_2'\delta(\mathbf{r}_m-\mathbf{r}_{m'})+\frac{\lambda z_m z_{m'}}{|\mathbf{r}_m-\mathbf{r}_{m'}|}-\frac{\lambda z_m z_{m'}\kappa'\varepsilon' T'}{\varepsilon T} . \tag{27}$$

Equation (26) shows that for $\varepsilon' T'>\varepsilon T$, the disorder-averaged potential of mean force between equally charged beads that includes both the direct Coulombic repulsion and the disorder-induced attraction exhibits a minimum at a distance $r_{\min}$ that satisfies the relation

$$1-\frac{\varepsilon' T'}{\varepsilon T}=(1+\kappa' r_{\min})e^{-\kappa' r_{\min}} . \tag{28}$$

The mean force between equally charged beads m and m' remains repulsive if the separation $|\mathbf{r}_m-\mathbf{r}_{m'}|$ is smaller than the distance $r_{\min}$. The force is, however, attractive when the two particles are separated by a distance $|\mathbf{r}_m-\mathbf{r}_{m'}|>r_{\min}$. Physically, the effect is explained by the fact that equally charged beads are attracted to the same potential wells created by a high density of oppositely charged disorder sites. At distances $r_{mm'}>r_{\min}$, this attraction prevails over the direct repulsion between the two units. A related phenomenon has been discussed previously in the context of colloidal solutions where the counterions are known to accumulate in potential wells adjacent to the macroions, the net result being an attractive potential of mean force between equally charged mobile ions in solution [64–66].

The dependence of the critical distance $r_{\min}$ [defined in Eq. (28)] on the ratio $\varepsilon' T'/\varepsilon T$ and on the screening parameter $\kappa'(T')$ of the disordered medium is illustrated in Fig. 1. Higher values of $\varepsilon' T'/\varepsilon T$ and κ' correspond to a shorter range of bead-bead repulsion and a faster crossover to the attractive interaction. The parameters $\varepsilon' T'/\varepsilon T$ and κ' will therefore have a significant effect on the behavior of the polyion. To minimize the Coulombic energy, the polyion will tend to assume configurations with typical bead-bead separations close to the distance $r_{\min}$, where $r_{\min}$ corresponds to the minimum of the disorder-averaged pair potential among the beads. This, in turn, favors configurations with the radius of gyration R_g close to the distance $r_{\min}$. For smaller coils, the Coulombic forces are expected to enhance the swelling of the polymer while they tend to suppress its growth beyond the size $R_g \sim r_{\min}$. These trends have important repercussions for the scaling behavior to be discussed in the following sections.

3. *Screened polyion in the presence of quenched charged disorder and mobile ions*

We now briefly consider a situation that is more general and perhaps more frequently encountered in practice

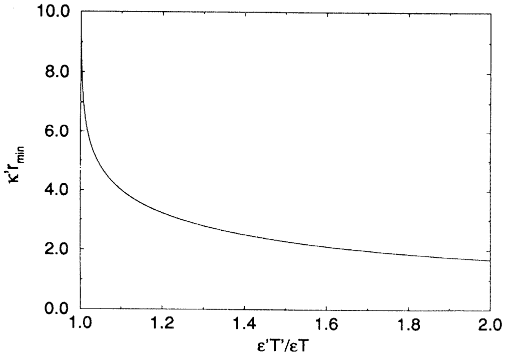

FIG. 1. The dependence of the characteristic distance $r_{\min}$ on the quenching conditions T' and $\varepsilon'(T')$ and on the density of the disorder measured in terms of the screening parameter $\kappa'(T',\varepsilon')$.

than the problem considered so far. Specifically, we look at situations where the electrostatic interactions among the polyion beads and those between the beads and the disorder charges are mitigated by the presence of a simple electrolyte characterized by its own screening parameter $\kappa(T)$. This entails the presence of additional mobile simple ions that are not attached to the fixed sites on the quenched irregular matrix. In the absence of the quenched charged disorder, the averaging over the electrolyte configurations results in screening of the bead-bead interactions. When the polyion and the salt are brought in contact with the quenched disordered medium, these screened bead-bead interactions are further modified upon integrating out the disorder. Following the procedure employed with bare Coulombic interactions between the beads and the disorder sites, we obtain the following expression for the disorder-averaged potential of mean force between the two beads m and m':

$$\bar{u}_{mm'}(\mathbf{r}_m-\mathbf{r}_{m'})=u_2'(\mathbf{r}_m-\mathbf{r}_{m'})-\sum_k\sum_{k'}z_kz_{k'}\int\int\frac{\lambda_{mk}}{|\mathbf{r}_m-\mathbf{r}_k|}\chi_{kk'}(\mathbf{r}_k-\mathbf{r}_{k'})\frac{\lambda_{m'k'}}{|\mathbf{r}_{m'}-\mathbf{r}_{k'}|}d\mathbf{r}_k d\mathbf{r}_{k'}\ , \tag{29}$$

where $u_2'(\mathbf{r}_m-\mathbf{r}_{m'})$ is given by Eq. (17) and the summations are over all ionic species k of the salt and the quenched medium. The double sums contain the terms which stem from site-site, site-ion, and ion-ion correlations. The density-density correlation functions $\chi_{kk'}(\mathbf{r}_k-\mathbf{r}_{k'})$ involving only quenched sites are not affected by the presence of the salt. The density-density correlation functions involving the salt ions are, however, affected by the presence of the quenched disorder. Formally, they can be determined by applying Eq. (10) to all species pairs, kk'. The total correlation functions $h_{kk'}(\mathbf{r}_k-\mathbf{r}_{k'})$ can be approximated by the negative of the reduced potential of mean force between species k and k', $-\bar{u}_{kk'}(\mathbf{r}_k-\mathbf{r}_{k'})$. These potentials can be calculated by using equations analogous to Eq. (29) which will, in this case, represent a system of integral equations [46,67,68] for $\bar{u}_{kk'}(\mathbf{r}_k-\mathbf{r}_{k'})$. These equations can be solved by any of the standard techniques of integral equation theory [52,53], a problem to which we hope to return in a separate study.

We have now developed expressions for the disorder-averaged pair interactions between the polyion beads. In the following, we apply these results to study polyion conformational statistics in charged disordered media. We do so by analyzing our equations approximately via a variational calculation, and by Monte Carlo simulations.

III. VARIATIONAL CALCULATION

Our analysis has reduced the problem of a polyelectrolyte in quenched disordered media to the simpler issue of treating a self-interacting chain with modified, disorder-averaged intramolecular forces In view of this result, the configurational statistics of the polyion can be obtained by various methods that have been devolved to study polymers in environments free of disorder. The averaging over polyion configurations involves the calculation of path integrals with the following "action" functional

$$H=\frac{3}{2l}\int_0^L ds\left[\frac{\partial\mathbf{r}(s)}{\partial s}\right]^2+\tfrac{1}{2}\int_0^L ds\int_0^L ds'\hat{u}[\mathbf{r}(s)-\mathbf{r}(s')]\ , \tag{30}$$

where $\hat{u}[\mathbf{r}(s)-\mathbf{r}(s')]$ represents the disorder-averaged bead-bead potential and s is the contour coordinate for a given unit on a chain of length L. A continuous representation is chosen for the sake of mathematical convenience. The propagator $G(\mathbf{R},L)$ corresponding to a given end-to-end vector $\mathbf{R}$ is then given by the expression

$$G(\mathbf{R},L)=\int_{\mathbf{r}(0)=0}^{\mathbf{r}(L)=\mathbf{R}}D[\mathbf{r}(s)]\exp\left\{-\frac{3}{2l}\int_0^L ds\left[\frac{\partial\mathbf{r}(s)}{\partial s}\right]^2-\tfrac{1}{2}\int_0^L ds\int_0^L ds'\int\frac{d^3\mathbf{k}}{(2\pi^3)}\tilde{u}(\mathbf{k})e^{i\mathbf{k}\cdot|\mathbf{r}(s)-\mathbf{r}(s')|}\right\}\ , \tag{31}$$

where $\tilde{u}(\mathbf{k})$ is the Fourier transform of the effective potential, $\hat{u}[\mathbf{r}(s)-\mathbf{r}(s')]$. The integrals in Eqs. (30) and (31) cannot be evaluated analytically but many approximate theories and simulation methods have been reported. To illustrate the effect of the disorder on the structure of a polyelectrolyte, we first apply a particular form of the standard variational method that is due to Muthukumar, who considered an isolated polyion in solution or at an electrified interface [16]. The method is based on the minimization of the well-known Gibbs-Bogoliubov free energy bound, $F_T\geq F$, with

$$F_T=F_0+\langle H-H_0\rangle_0\ . \tag{32}$$

H is the true Hamiltonian of Eq. (30) for our model system, and F the corresponding free energy. H_0 is a harmonic reference Hamiltonian, and $F_0=\ln\operatorname{Tr}\exp(-H_0)$ the free energy of the reference system. The angular brackets $\langle\ \rangle_0$ denote a canonical average with respect to the Hamiltonian H_0. The configuration-averaged pair interactions between the beads s and s', $\langle\hat{u}_{ss'}\rangle$, contained in the average $\langle H\rangle$ are then easily calculated after the usual plane-wave expansion of the potentials $\hat{u}[\mathbf{r}(s)-\mathbf{r}(s')]$ to be

$$\langle \hat{u}_{ss'} \rangle = \frac{1}{2\pi^2} \int \left\{ u_2' + \frac{4\pi\lambda}{k^2} - \frac{(4\pi\lambda)^2}{k^2} \frac{\rho_e}{k^2+\kappa'^2} \right\} \exp\left[-\frac{k^2}{6} \langle |\mathbf{r}(s)-\mathbf{r}(s')|^2 \rangle \right] k^2 dk$$

$$= \left[\frac{3}{2\pi} \right]^{3/2} u_2' \langle |\mathbf{r}(s)-\mathbf{r}(s')|^2 \rangle^{-3/2} + \frac{\lambda\sqrt{6}}{\sqrt{\pi}} \langle |\mathbf{r}(s)-\mathbf{r}(s')|^2 \rangle^{-1/2}$$

$$- \frac{4\pi\rho\lambda^2}{\kappa'} \operatorname{erfc}\left[\frac{\kappa' \langle |\mathbf{r}(s)-\mathbf{r}(s')|^2 \rangle^{1/2}}{\sqrt{6}} \right] \exp\left[\frac{\kappa'^2 \langle |\mathbf{r}(s)-\mathbf{r}(s')|^2 \rangle}{6} \right] . \quad (33)$$

In several applications, Gaussian variational methods have been shown to overestimate the short-ranged steric effects [25,69,70] but this problem is mitigated by the use of a suitably restricted reference Hamiltonian H_0 [16]. Moreover, Bouchaud *et al.* [20] have demonstrated that the method is, in general, fairly accurate for systems dominated by long-ranged electrostatic interactions since the structure of these systems is described adequately by a Gaussian Hamiltonian. The reference Hamiltonian used in Ref. [16] has the form of the ideal elasticity term of Eq. (31) with modified step length, l_1, replacing the unperturbed length, l. Expanding the expressions for the chain propagator and the corresponding free energy [16] in the plane wave, q, and further assuming the dominance of the lowest mode of q, the standard minimization procedure leads [16] to the following approximate relation for the mean-squared radius of gyration of the polyion, $R_g^2 = 1/(2N^2)\sum_m \sum_{m'} \langle |\mathbf{r}(m)-\mathbf{r}(m')|^2 \rangle$:

$$R_g^2 = L l_1 / 6 ,$$

l_1 being the solution of the equation

$$\left[\frac{1}{l} - \frac{1}{l_1} \right] = \frac{1}{18 L l^2} \int_0^L ds \int_0^L ds' \int \frac{d^3k}{(2\pi)^3} \tilde{u}(k) k^2 |s-s'|^2 e^{-k^2 l_1 |s-s'|/6} . \quad (34)$$

For details of the derivation of Eq. (34) as well as a discussion of the adopted approximations, the reader is referred to the original work of Muthukumar [16]. We solve Eq. (34) using the Fourier transform of the effective potential of mean force between the beads embedded in charged disordered medium, $\hat{u}$ [see Eq. (26)]; specifically,

$$\tilde{u}(k) = u_2' + \frac{4\pi\lambda}{k^2} - \frac{4\pi\lambda\kappa'^2}{k^2(k^2+\kappa'^2)} \frac{\varepsilon' T}{\varepsilon T} . \quad (35)$$

The integration of Eq. (34) with the potential $\tilde{u}(k)$ given by Eq. (35) leads to the following result:

$$\left[\frac{1}{l} - \frac{1}{l_1} \right] = \frac{4}{3} \left[\frac{3}{2\pi} \right]^{3/2} \frac{u_2'}{l^2 l_1^{5/2}} L^{1/2} + \frac{6^{1/2}}{45\pi^{1/2}} \frac{4\lambda}{l^2 l_1^{3/2}} L^{3/2} \left[\frac{\varepsilon T - \varepsilon' T'}{\varepsilon T} \right]$$

$$+ \frac{6^{1/2}}{3\pi^{1/2}} \frac{4\lambda}{l^2 l_1^{3/2}} L^{3/2} \frac{\varepsilon' T'}{\varepsilon T} \left\{ \frac{\pi^{1/2} e^b}{2 b^{5/2}} (b^2 - 4b + 6) \operatorname{erfc}(b^{1/2}) - \frac{3\pi^{1/2}}{b^{5/2}} - \frac{\pi^{1/2}}{b^{3/2}} + \frac{6}{b^2} \right\} , \quad (36)$$

where $b = \kappa'^2 L l_1 / 6$. The first term in the above expression represents the excluded volume effect and the remaining two terms comprise the direct and the disorder mediated electrostatic interactions for arbitrary disorder concentration and the quenching conditions, T' and ε'. In actual quenched systems, only situations with $T' > T$ are encountered. For the sake of comparison with earlier work, it is, however, also interesting to consider the limit $\varepsilon' T' \rightarrow \varepsilon T$. In this hypothetical case, the second term on the right-hand side of Eq. (36) vanishes and the third term approaches the result [16,22] for the polyion in a simple electrolyte solution with the screening parameter $\kappa' \rightarrow \kappa$. In the absence of electrostatic effects, Eq. (36) is identical to the result of the variational replica analysis of Ref. [43] carried out by using the present reference Hamiltonian. For repulsive u_2', it leads to the known Flory relation with scaling exponent, $2\nu = 6/5$ [16]. For a polyion in a very weak disorder, the scaling appropriate for a nonscreened polyelectrolyte (ν close to 2) is recovered. The presence of quenched charged disorder leads to additional, attractive forces between the polyion beads. At $\varepsilon' T' \rightarrow \varepsilon T$, this would merely screen the existing repulsions, the strong screening limit coinciding with the case of an uncharged self-avoiding macromolecule At $\varepsilon' T' > \varepsilon T$, however, the disorder-induced attractive contribution can exceed the direct Coulombic repulsion between the ionized beads leading to an overall coil size that is smaller than that of a neutral polymer. At these conditions, the chain will behave in a manner qualitatively different from the case of a screened polyelectrolyte considered in Ref. [16]. For this to happen, the typical bead-bead separation should exceed the distance $r_{\min}$ corresponding to the minimum of the effective pair potential among the beads. For bead pairs at smaller separations, the repulsive interactions dominate. This suggests that two different scaling regimes of the polyelectrolyte in the disordered medium should exist. The properties of relatively short polyions with $R_g < r_{\min}$ are expected to resemble those of screened polyelectrolytes in ordinary solutions. The size of longer polyions with radius of gyration exceeding the distance $r_{\min}$, will, however, be controlled by the balance between short-ranged repulsions and the long-ranged attraction among the beads. In the former regime, the polyion size will grow relatively rapidly with the contour length L. In the latter regime, an essentially slower growth is expected. The crossover between the two regimes is expected at or near the degree of polymerization at which R_g approaches the critical distance $r_{\min}$. In view of Eq. (28) and Fig. 1, the length at which the crossover occurs can be shortened by increasing the quenching temperature T' and the density of the disorder ρ_e. This is explained by enhanced potential fluctuations corresponding to higher values of ρ_e and the product $\varepsilon' T'$. We shall make these statements precise when we discuss the physical meaning of our numerical results to be presented in Sec. V.

IV. MONTE CARLO SIMULATION

We have carried out Monte Carlo simulations of a model polyelectrolyte characterized by a disorder-averaged polymer Hamiltonian that is essentially equivalent to that used in the variational analysis. The purpose of these simulations is to examine the accuracy of the approximate variational calculations. This involves lengthy but tractable computations. Explicit consideration of numerous realizations of quenched disorders with long-ranged interactions, on the other hand, would require extreme computational resources. According to Eq. (14), the Hamiltonian is comprised of the energy associated with harmonic bonds between the neighboring beads, the excluded volume term, and the disorder-averaged interactions described by Eq. (26). In contrast with our preceding analytical treatment, for the simulations, the excluded volume term is described in terms of a true hard-core potential

$$u_{\text{hc}}(\mathbf{r}_m - \mathbf{r}_{m'}) = \infty \quad \text{if } |\mathbf{r}_m - \mathbf{r}_{m'}| < \sigma \\ = 0 \quad \text{otherwise} \tag{37}$$

with the hard-core diameter σ chosen to match the value of the excluded volume parameter $u_2 = 4\pi\sigma^3/3$ used in the analytical treatment. No steric disorder obstacles were considered in the Monte Carlo simulations. Apart from the disorder-induced Coulombic term described by Eq. (26), the above model is identical to the one used in recent Monte Carlo studies of an ordinary polyelectrolyte in solution [28,29]. The simulations, initiated from a random polyion configuration, were performed according to the standard Metropolis algorithm. The attempted moves consisted of random displacements of individual beads and forward or backward reptation moves [71] involving either of the two end groups without altering the configuration of the rest of the chain. The allowed displacement and the fraction of reptation moves were adjusted to secure acceptance of the moves between the limits of 40–60 %. Statistical accuracy was monitored by using the method of subaverages [72]. The number of configurations needed to obtain reproducible results varied with the length of the chain. Typically, we needed about 10^4 attempted moves per bead during equilibration, while a total of about 10^5 attempted moves per bead were sufficient to obtain results for R_g with a standard deviation below 1–2 %. Above, the number of attempted moves *per bead* denotes the number of simulation sweeps. The total number of attempted chain configurations in a run is obtained by multiplying the number of sweeps by the number of beads N of the simulated polymer. About ten times longer runs would be needed to obtain a comparable accuracy for calculated squared end-to-end distances of the polyion.

V. RESULTS AND DISCUSSION

In this section, we present numerical results of our variational calculations and Monte Carlo simulations for the polyion size at different disorder strengths as measured by the quenching parameters T' and ε' and the average concentration of sites that comprise the disordered medium. We focus attention on situations wherein $\varepsilon' T' > \varepsilon T$. The model parameters used in most of our calculations correspond to a polymer containing 400 monomer units of length $l = 7.14$ A and a hard-core diameter $\sigma = 5$ A or, equivalently, $u_2 \sim 5.24 \times 10^2$ A^3. Each unit carries an elementary charge $q = e_0$. The product of the relative permittivity ε_r and the temperature T is taken to be 2.335×10^4, and we treat the disorder sites as point charges of magnitude $\pm e_0$. No steric obstacles are

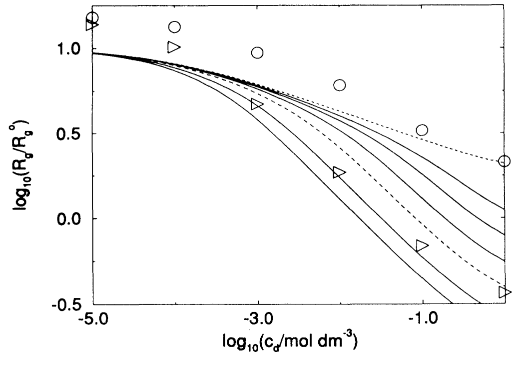

FIG. 2. The radius of gyration of a polyion containing 400 segments of length $l = 7.14$ A and charge $q = e_0$ at $\varepsilon_r T = 2.335 \times 10^4$ as a function of the density of the charged disorder c_d at different ratios between the quenching and the actual values of the products of the temperature and the permittivity (from top to bottom) $\varepsilon' T'/\varepsilon T = 1.0$ (○, dotted line), 1.025, 1.05, 1.1, 1.2 (△, dashed line), 1.5, or 2. The symbols denote the simulation results and the lines describe the predictions of the variational approach.

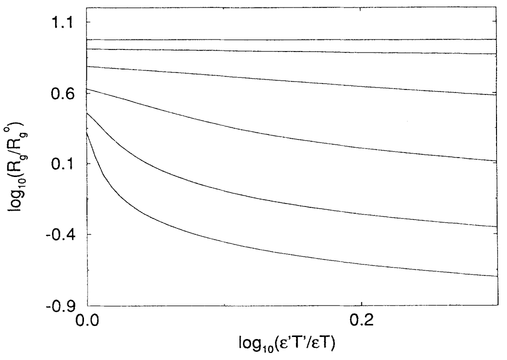

FIG. 3. The radius of gyration of the polyion as a function of the product of the quenching temperature T' and the permittivity $\varepsilon'(T')$ at different disorder densities (from top to bottom) $c_d=10^{-5}$, 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}, or 1.0 mol dm^{-3}.

present in our system. Figures 2 and 3 illustrate the dependence of the radius of gyration, R_g, on the concentration of the ionic sites of the disorder, c_d, and on the quenching parameter $\varepsilon'T'$. As seen from Fig. 2, at low disorder density the chain assumes a relatively extended configuration whose end-to-end distance rapidly decreases with both the density and with the product of the quenching temperature T' and the permittivity $\varepsilon'(T')$ of the disorder. In the hypothetical case with $\varepsilon'T'=\varepsilon T$, the average size of the coil measured in terms of R_g exceeds the value $R_g^0=\sqrt{Ll/6}$ characteristic of an ideal Gaussian coil at all disorder concentrations c_d. The situation is, however, qualitatively different in situations with $\varepsilon'T'>\varepsilon T$. When $\varepsilon'T'$ exceeds the value of εT for the actual system by as little as 15–20 %, the attractive disorder-induced contributions prevail over the direct electrostatic repulsion between the beads for disorder densities greater than $\sim 10^{-1}$ mol dm^{-3}. Further increase in c_d leads to a pronounced contraction of the polyion coil whose average diameter may be orders of magnitude smaller than in the absence of the disorder. Figure 3 presents the dependence of R_g on $\varepsilon'T'$ at various disorder densities c_d. At low c_d, the product of the quenching temperature T' and the permittivity $\varepsilon'(T')$ is, of course, of little importance. At higher densities, however, the value of $\varepsilon'T'$ has a notable effect on the structural behavior of the chain. Here, we observe a transition from swollen to contracted coil as $\varepsilon'T'$ is increased from values around to values above that of the actual system at the temperature T. Of course, we note that only temperatures $T'>T$ correspond to physically realistic situations involving quenched disorders. The physical origin of the dependence of the effect of the disorder upon the quenching temperature can be seen clearly by considering the spatial fluctuations in the electric field in a quenched disordered medium. As shown in a different context [50], the mean-square fluctuation in the electrostatic potential, $\langle \delta\phi^2 \rangle$, is related to fluctuations in the density of the charged disorder in the following manner:

$$\begin{aligned}
\langle \delta\phi^2 \rangle &= \lim_{\mathbf{r}\to\mathbf{r}'} \langle \delta\phi(\mathbf{r})\delta\phi(\mathbf{r}') \rangle \\
&= \lim_{\mathbf{r}\to\mathbf{r}'} \int d\mathbf{r}'' \int d\mathbf{r}''' \frac{e_0^2}{4\pi\varepsilon|\mathbf{r}-\mathbf{r}''|} \\
&\qquad \times \chi(\mathbf{r}-\mathbf{r}') \frac{e_0^2}{4\pi\varepsilon|\mathbf{r}'-\mathbf{r}'''|} \\
&= \lim_{\mathbf{r}\to\mathbf{r}'} \frac{\rho_d e_0^4}{4\pi\varepsilon^2\kappa'^2} \left[\frac{1}{|\mathbf{r}-\mathbf{r}'|} - \frac{e^{-\kappa'|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \right] \\
&= \frac{\rho_d e_0^4}{4\pi\varepsilon^2\kappa'} \sim \sqrt{\varepsilon'T'} \, ,
\end{aligned} \tag{38}$$

i.e., $\langle \delta\phi^2 \rangle$ is a monotonically increasing function of the product of the quenching temperature T' and the concomitant permittivity ε'. For sufficient field fluctuations, the tendency towards localization in favorable regions of the field may prevail over the intramolecular repulsions among the beads leading to a crossover in the scaling of polyion coil size. This will be discussed in some detail shortly.

Inspection of simulation data included in Fig. 2 leads to conclusions similar to those obtained from the variational calculation. The comparison between the results of the two methods applied to essentially equivalent model Hamiltonians reveals a fair agreement within the whole range of the disorder densities considered. In a number of additional simulations corresponding to the conditions of Fig. 2 (not shown), the present spring-bead model of the polyion was replaced by the model with fixed bonds of length l. These calculations lead to somewhat smaller coil sizes (R_g) at low c_d but no qualitative changes in the polyion behavior were observed as a result of this modification.

The dependence of the coil size on the contour length of the polymer, L, is usually characterized by the scaling exponent, $2\nu(L)=d\ln R_g^2/d\ln L$. The effects discussed above are reflected clearly upon examining the variation of ν with c_d and $\varepsilon'T'/\varepsilon T$. As mentioned earlier, 2ν is close to 2 in highly dilute systems. In concentrated disorder and with $\varepsilon'T'=\varepsilon T$, the behavior of the polymer is similar to that of a neutral self-avoiding chain. In quenched disorders with $\varepsilon'T'>\varepsilon T$, however, we find a drastic reduction of the scaling exponent ν under certain conditions. In view of the discussion presented in Sec. II B 2, this crossover is expected when the size of the polyelectrolyte coil R_g approaches the critical distance $r_{\min}$ corresponding to the minimum in the disorder-averaged pair potential among the beads. The crossover is, therefore, facilitated by increasing the disorder concentration c_d and the product $\varepsilon'T'$ (see Fig. 2).

The crossover between different scaling regimes can be interpreted in terms of the equilibrium between opposing attractive and repulsive contributions represented by different terms in Eq. (36). For coils characterized by the radius of gyration $R_g<r_{\min}$, the chain behavior should be dominated by the balance between the bare elasticity term and the electrostatic repulsive term of Eq. (36). The first term is a constant equal to $1/l$, and the form of the second term, represented by the last two contributions at

the right-hand side of Eq. (36), depends on the concentration of the disorder. At sufficiently large c_d and κ', it is dominated by the last term of Eq. (36) which varies approximately as $L^{1/2}/l_1^{5/2}$ [16]. The balance between the above two terms requires that $1/l \sim L^{1/2}/l_1^{5/2}$, $l_1 \sim L^{1/5}$, and $R_g^2 \sim Ll_1 \sim L^{6/5}$. Short polyions ($R_g < r_{\min}$) in concentrated disordered medium assume the behavior of the Flory's self-avoiding polymer. At very small c_d, κ', and $R_g < r_{\min}$, on the other hand, the sum of the last two terms in Eq. (36) gives a repulsive term varying as $L^{3/2}/l_1^{3/2}$. Here, the balance requirements lead to the relation $1/l \sim L^{3/2}/l_1^{3/2}$, $l_1 \sim L$, and $R_g^2 \sim Ll_1 \sim L^2$. At low disorder densities, short polyions resemble nonscreened polyelectrolytes in solution.

For coils whose size exceeds the characteristic distance $r_{\min}$, a significant fraction of the bead pairs experiences an attractive disorder-induced interaction. At these conditions, the structure of the chain reflects an equilibrium between the attractive and repulsive Coulombic contributions represented by the second and the third term on the right-hand side of Eq. (36). The balance between these two terms requires that $L^{3/2}/l_1^{3/2} \sim L^{1/2}/l_1^{5/2}$, $R_g^2 \sim Ll_1$ be approximately constant ($\nu \sim 0$), and the size of the coil be virtually independent of L. An analogous behavior has been observed in earlier studies of self-avoiding polymers embedded in a concentrated medium comprising disordered steric obstacles [39–48].

These trends are illustrated by the numerical results presented in Figs. 4 and 5. Figure 4 shows the concentration dependence of the scaling exponent ν calculated according to Eq. (36) for different values of the parameter $\varepsilon'T'/\varepsilon T$, and a constant degree of polymerization $N = 4 \times 10^2$. At sufficiently low concentration c_d, the characteristic distance $r_{\min}$ of Eq. (28) will exceed the coil size R_g. For these conditions, the dominant balance analysis of the preceding paragraphs predicts that 2ν will approach 2, the value characteristic of a strongly extended polyion. The variational results for low c_d clearly conform with this exception. At a higher density c_d, on the other hand, the value $r_{\min}$ becomes comparable to the radius of gyration R_g. The attractive disorder-averaged interactions that are in effect in this regime give rise to a notable decrease in the scaling exponent ν. The density at which this happens depends on the parameter $\varepsilon'T'/\varepsilon T$. At high densities c_d, the exponent ν becomes arbitrarily small for all $\varepsilon'T' > \varepsilon T$.

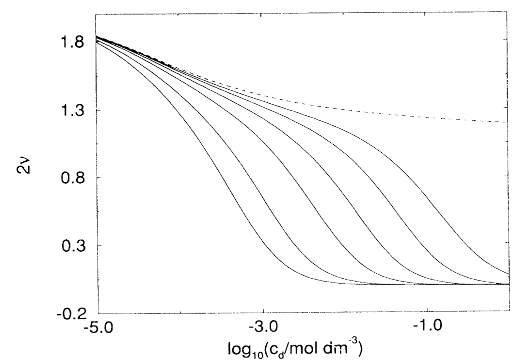

FIG. 4. The differential scaling exponent $2\nu = d\ln\langle h^2\rangle / d\ln L$ of the polyion containing 400 monomer units of length $l = 7.14$ A and charge $q = e_0$ at $\varepsilon_r T = 2.335 \times 10^4$ as a function of the disorder density c_d at different ratios $\varepsilon'T'/\varepsilon T$ (from top to bottom): $\varepsilon'T'/\varepsilon T = 1.0$ (dashed line), 1.025, 1.05, 1.1, 1.2, 1.5, or 2.

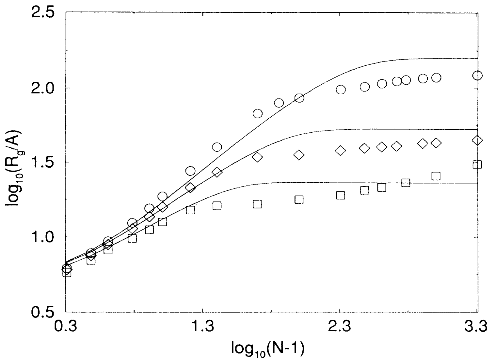

FIG. 5. Radius of gyration as a function of the number of links, $N-1$, at disorder densities (from top to bottom) $c_d = 0.01$ (○), 0.1 (◇), or 1 mol dm^{-3} (□) at $\varepsilon'T'/\varepsilon T = 1.2$. The symbols correspond to the simulation results and the lines denote the predictions of the variational method.

Figure 5 illustrates the dependence of the average size of the coil on the number of links in the chain, $N-1$, at three different concentrations of the disorder $c_d = 0.01$, 0.1, or 1.0 mol dm^{-3} and at $\varepsilon'T' = 1.2\varepsilon T$. The variational and the simulation results ar included. At small values of N, R_g is generally smaller than the distance $r_{\min}$ estimated by Eq. (28) for a specified concentration. In this regime, the calculated slopes ν are close to the value $2\nu \sim 6/5$ predicted by the above scaling analysis, although we expect the dominant balance argument to be less reliable at very low values of N. With increasing N, the size of the coil R_g increases until it becomes comparable to the distance $r_{\min}$ characteristic for given concentration. When this is the case, the slope ν gradually falls to a value close to zero in the case of the variational model while the simulation results seem to retain a small but finite slope (ν between 0.06 and 0.09). The values of $r_{\min}$ obtained from Eq. (28) for the three concentrations in Fig. 5 correspond to $\log_{10}(r_{\min}/\mathrm{A}) \sim 2.03$, 1.53, and 1.05, respectively. The simulation results for the value of R_g at which the crossover occurs are in a very good agreement with these predictions (see Fig. 5); the crossover takes place at somewhat larger values of R_g in the case of the variational calculations.

A physical rationale for the virtual independence of R_g on L observed in the regime of high c_d and $\varepsilon'T'$ is that, at sufficient disorder strength, the whole chain tends to localize within potential wells containing an excess of oppositely charged particles of the disorder. In this way, the radius of gyration of the collapsed coil remains comparable to the typical size of the wells related to the screening length $\kappa'(T')^{-1}$. For strongly contracted coils, of course, packing forces should ultimately prevail over the purely electrostatic localization. Thus, the true limiting value of ν is expected to be close to $\frac{1}{3}$. We have observed such a transition in our Monte Carlo simulations for long chains $(2\times10^2 \leq N \leq 2\times10^3)$ at the highest concentration of the disorder charges that we consider. An analogous transition is, however, not seen in the variational results for this high concentration. The present variational calculations, based on the asymptotic low-density form of the excluded volume interactions [Eq. (2)], cannot capture packing effects in this limit [43,48]. The applicability of the present theory is, therefore, restricted to systems with moderate packing densities of polymer segments in the coil. For chain lengths considered in Fig. 5, $N\sim 2\times 10^3$, this is no longer the case at the highest density of the disorder, $c_d = 1$ mol dm^{-3}. At higher degrees of polymerization, N, the critical packing density will, of course, be reached at even lower disorder density and vice versa. The issue of including higher-order repulsive terms to model the repulsive interactions has been addressed within the context of the variational model of Ref. [43]. Therein, the balance between the short-ranged disorder-induced attraction and the intramolecular three-body term has been shown to lead to the correct high-density scaling $\nu\sim\frac{1}{3}$. If applied to our present system, the same procedure results in an additional repulsive term $\sim u_3/l_1^4$ [43] to be added to the right-hand side of Eq. (36). Here, u_3 corresponds to the three-body cluster integral which, for hard spherical particles, is of the order of u_2^2 [52]. The balance between this three-body term and the disorder-induced attractions varying as $L^{3/2}/l_1^{3/2}$ requires l_1 to vary as $L^{-3/5}$ or, equivalently, $R_g \sim L^{1/5}$. At extremely high densities of the ionic disorder, this result is indeed recovered when we perform calculations based on Eq. (36), supplemented by the three-body term of arbitrary strength, $u_2^2/l^3 l_1^4$. The deviation from the close-packing exponent $\nu\sim\frac{1}{3}$ may be related to the fact that disorder-induced attractions do not extend to the nearest proximity of the particles but rather gradually turn to repulsion at distances $r<r_{\min}$. Our results may be further affected by the approximations inherent to the variational method with the reference Hamiltonian imposing a Gaussian intramolecular distribution. Such calculation is expected to be inaccurate when short-ranged repulsive interactions dominate the chain behavior [64,68] and cannot adequately describe the formation of distinct blobs that would occur in the absence of the attractive regions that are sufficiently big to accommodate the whole polymer. In spite of these limitations of the Gaussian variational method that become important at extreme strength of the disorder, useful insights into disorder-induced polyion contraction appear to be provided by the present approach. This is demonstrated by the comparison of the variational calculations with our Monte Carlo simulations. A field-theoretic analysis that treats the short-ranged features less approximately is currently under way, and will be reported in a forthcoming communication.

VI. CONCLUDING REMARKS

In this paper, we have studied the effects of charged disordered media on the structure of an isolated ionized macromolecule. Our analysis is based on the equivalence between the effects of quenched disorder and annealed disorder in the adiabatic limit. Based on this equivalence, we derive expressions for the disorder-averaged pair potentials between the polyion beads in the presence of random obstacles or ionic sites that have been quenched at a certain temperature that is higher than the temperature of observation. As a result of the charge-density fluctuations in the system, the effective interaction between equally charged beads displays a minimum at a characteristic distance $r_{\min}$ and is attractive at large separations. This feature is explained by the attraction of the beads to the same potential wells created by the accumulation of oppositely charged ionic sites of the quenched disorder. The polyion tends to reduce its Coulombic energy by assuming configurations that favor bead-bead distances close to the optimal distance $r_{\min}$. The magnitude of $r_{\min}$ decreases with increasing density of ionic sites and with the quenching temperature T' of the disordered medium. These parameters, therefore, have a notable effect on the structure of the polyion. For polyelectrolyte coils with radius of gyration R_g exceeding $r_{\min}$, the attractive disorder-induced interactions among the beads suppress further swelling of the polyion. This is reflected in a change in the structural behavior of the polyion that takes place when its size reaches the magnitude $R_g \sim r_{\min}$. The radius of gyration of smaller coils scales with the degree of polymerization N in a similar way as in the case of the polyion in the absence of quenched disorder. The size of the polyions with coil size $R_g > r_{\min}$, however, becomes very weakly dependent on N. This crossover in the polyion scaling behavior near $R_g \sim r_{\min}$, predicted on the basis of the above physical considerations, is captured by an approximate variational theory and is seen in Monte Carlo simulations carried out using the same disorder-averaged Hamiltonian of the polymer

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