

# Monte Carlo simulations of a hydrophobic weak polyelectrolyte. Charge distribution as a function of conformation

J. L. F. Abascal,<sup>a)</sup> Alexander P. Sassi, Harvey W. Blanch, and John M. Prausnitz<sup>b)</sup>  
*Chemical Engineering Department, University of California and Chemical Sciences Division, Lawrence  
Berkeley Laboratory, Berkeley, California 94720*

(Received 26 April 1993; accepted 28 May 1993)

The conformational behavior of an individual polymer chain determines many of its solution properties. For polyelectrolytes, the electrostatic interactions give rise to a rich variety of solution properties that are important in biological systems and in technological applications. We have recently used a lattice-model representation of a polyelectrolyte to study pH-induced structural transitions in hydrophobic, weak polyelectrolytes. For simulations in the grand-canonical ensemble, the ionization state of each of the ionizable segments is not constant but fluctuates in response to the local charge environment. The charge density is, therefore, not necessarily uniform because the charges may be unevenly distributed, depending on the local environment. We report briefly the charge distribution obtained from grand-canonical simulations of a hydrophobic, weak polyelectrolyte.

The model and simulation method used in this work are described in Refs. 1 and 2. The polymer is represented as a self-avoiding walk of  $N$  ( $=40$ ) segments on a cubic lattice. The fraction of potentially ionizable beads  $\lambda$  is 0.325 for comparison to previous work.<sup>2</sup> The interaction between ionized segments is described by a screened Debye-Hückel coulombic potential.<sup>2</sup> Nonbonded nearest-neighbor segments interact with a fixed potential  $\epsilon$ ; we only consider the case  $\epsilon \leq 0$  to represent polymer hydrophobicity. The configurations were obtained using the Metropolis Monte Carlo method and recorded every 3000 attempted moves. Details of the simulations are given in our previous paper.<sup>2</sup>

To characterize the charge distribution, we define the function  $q(r)$  as the quotient of the intramolecular distribution function for charged segments [ $g_{\text{intra}}^{\text{ch}}(r)$ ] and that for all segments, irrespective of ionization state [ $g_{\text{intra}}(r)$ ]:

$$q(r) = g_{\text{intra}}^{\text{ch}}(r) / g_{\text{intra}}(r),$$

where  $g_{\text{intra}}^{\text{ch}}(r)$  is the ensemble average of the number of charged segments at distance  $r$  normalized to the number of sites at  $r$  and  $g_{\text{intra}}(r)$  is the ensemble average of the number of segments at  $r$  normalized to the number of sites at  $r$ . The charge distribution  $q(r)$  therefore gives the probability that a segment at distance  $r$  from the center of mass is charged. The mean ionization of the chain,  $\alpha$ , is then given by

$$\alpha = \frac{1}{N} \int g_{\text{intra}}^{\text{ch}}(r) r^2 dr,$$

where  $N$  is the number of segments in the chain.

Figure 1 presents the charge distribution  $q(r)$  as a function of  $r$  nondimensionalized by the lattice length,  $l$ , for  $\text{pH} - pK_0 = -2.5$  and the cases  $\epsilon/kT = 0$ ,  $\kappa^{-1} = 9.62 \text{ \AA}$  ( $0.1M$ ),  $\epsilon/kT = -1.0$ ,  $\kappa^{-1} = 9.62 \text{ \AA}$  ( $0.1M$ ) and  $\epsilon/kT = 0$ ,  $\kappa^{-1} = 96.2 \text{ \AA}$  ( $0.001M$ ), where  $\kappa^{-1}$  is the Debye length, and  $M$  refers to the molarity of a 1-1 electrolyte. The cutoff of  $q(r)$  in these figures is at the distance which includes, on average, approximately 95% of the segments. As all the curves correspond to chains with the same number of segments, the mean rigidity of the polyelectrolyte at any state is reflected in the maximum value of  $r$  displayed in the corresponding plot. The mean ionization  $\alpha$  is shown as a dashed line reaching each curve.

As previously reported,<sup>2</sup> there is a close relationship between chain conformation (chain stiffness) and  $\alpha$ . The same holds for the shape of the  $q(r)$  curves. Despite the wide variety of conditions studied, the distribution of charges around the center of mass is determined essentially by chain stiffness. If the overall conditions lead to a highly ionized polyelectrolyte, the chain assumes an expanded conformation because of electrostatic repulsion between charged groups. In the limiting case of linear (or staircase) conformations, these repulsive interactions should produce a uniform distribution of charges along the chain. In the absence of hydrophobicity and at a pH such that most ionizable segments are protonated, a nearly uniform charge density is observed as in the case  $\epsilon/kT = 0$ ,  $\kappa^{-1} = 9.62 \text{ \AA}$  in Fig. 1. For this case, the value of  $q(r)$  is roughly equal to the maximum attainable ionization of 0.325, and  $q(r)$  falls at higher values of  $r/l$  because the outermost segments are not ionizable.<sup>2</sup> The maximum value of  $r/l$  for a staircase conformation is  $(N/6)\sqrt{3} = 10.5$  for a 40-segment chain, which is approximately the maximum value of  $r$  for the case  $\epsilon/kT = 0$ ,  $\kappa^{-1} = 9.62 \text{ \AA}$  in Fig. 1.

The opposite situation is that of compact chain conformation due to low chain ionization, hydrophobic forces and/or highly screened electrostatic interactions (high ionic strength). In these cases, the charges are preferentially located near the surface of the chain whereas the inner segments are mostly uncharged. Consequently,  $q(r)$  exceeds  $\alpha$  for all but the smallest values of  $r$ . Most cases are intermediate between the two aforementioned extremes. As the chain expands, the charge distribution  $q(r)$  tends to flatten. We also studied the effect of number of chain segments (results not shown) at the same ionic strength and pH. The mean ionization of a chain with 100 segments is approximately the same as that for 40 segments but, since the 100-segment chain is larger, there is a redistribution of

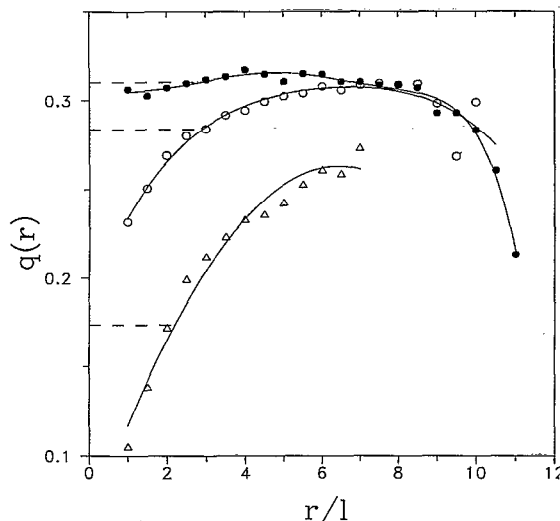


FIG. 1. Charge distribution as a function of distance to the center of mass for  $\text{pH} - \text{p}K_0 = -2.5$ . Closed circles denote the case  $\epsilon/kT=0$ ,  $\kappa^{-1}=9.62$  Å ( $0.1M$ ); Open circles denote the case  $\epsilon/kT=-1$ ,  $\kappa^{-1}=9.62$  Å ( $0.1M$ ); Triangles denote the case  $\epsilon/kT=0$ ,  $\kappa^{-1}=96.2$  Å ( $0.001M$ ). Dashed lines show the mean ionization  $\alpha$  for the corresponding conditions. Full lines are a guide to the eye.

charges toward the surface, and the shape of  $q(r)$  is flattened.

The variables of the system ( $\lambda$ ,  $\epsilon/kT$ ,  $\kappa$ ,  $\text{pH}$ ,  $\text{p}K_0$ ) in concert determine polymer ionization and conformation. However, once ionization and conformation are known, it appears possible to describe approximately the distribution of charges in a manner independent of the conditions by which the chain achieved its ionization and conformation, as shown in Fig. 2. Here the ratio of  $q(r)$  to its mean value,  $\alpha$ , is plotted as a function of radial distance reduced with the square root of the mean square radius of gyration,  $\langle s^2 \rangle^{0.5}$ . All curves cross approximately at the point (1,1) indicating that, for any combination of system variables, the average charge at a radial distance representing the mean extension of the chain is the mean ionization. The changes in shape of the curve are gradual and can essentially be defined by the initial slope, which is related to  $\alpha$  and  $\langle s^2 \rangle$ . We did not attempt to correlate the initial slope to  $\alpha$  and  $\langle s^2 \rangle$  because of the large number of systems needed for such a study.

We have examined the radial distribution of charges for a lattice-model, hydrophobic, weak polyelectrolyte using Monte Carlo simulation methods. If the polymer chain

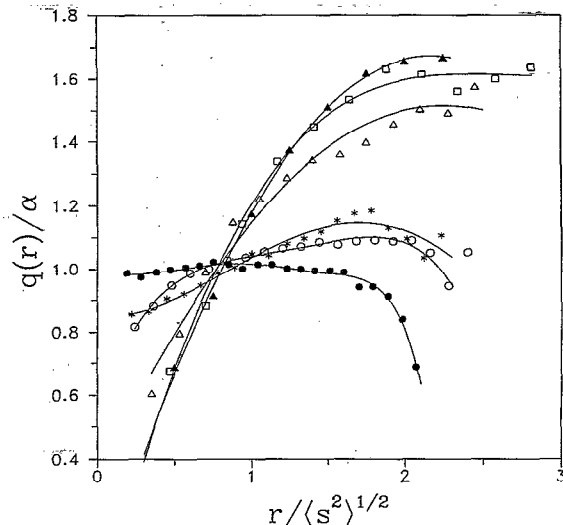


FIG. 2. Charge distribution relative to mean ionization as a function of radial distance reduced with the square root of the mean square radius of gyration. Data from Fig. 1 are plotted (using the same symbols) along with data for  $\text{pH} - \text{p}K_0 = -1$ . Asterisks denote the case  $\epsilon/kT=0$ ,  $\kappa^{-1}=9.62$  Å ( $0.1M$ ). Squares denote the case  $\epsilon/kT=-1$ ,  $\kappa^{-1}=9.62$  Å ( $0.1M$ ). Triangles denote the case  $\epsilon/kT=0$ ,  $\kappa^{-1}=96.2$  Å ( $0.001M$ ).

is highly collapsed, the charges are clustered predominantly on the surface, and the surface ionization is significantly greater than the average ionization,  $\alpha$ . If, however, the charge density is sufficient to expand the chain into a staircase conformation, the charge density is almost constant throughout the chain.

We thank the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy for financial support under Contract No. DE-AC03-76SF00098, Additional support was provided by the National Institutes of Health. J.A. is grateful to the Fundacion del Amo administered by the Universidad Complutense de Madrid, Spain, for a grant; A.S. to the University of California for a predoctoral fellowship; and all authors to Ronald A. Siegel at the University of California, San Francisco, for helpful comments.

<sup>a)</sup>Present address: Departamento de Química Física, Facultad Químicas, Ciudad Universitaria, 28040 Madrid, Spain.

<sup>b)</sup>To whom correspondence should be addressed.

<sup>1</sup>H. H. Hooper, S. Beltrán, A. P. Sassi, H. W. Blanch, J. M. Prausnitz, and R. A. Siegel, *J. Chem. Phys.* **93**, 2715 (1990).

<sup>2</sup>A. P. Sassi, S. Beltrán, H. H. Hooper, H. W. Blanch, J. M. Prausnitz, and R. A. Siegel, *J. Chem. Phys.* **97**, 8767 (1992).