Structure of Salt-Free Linear Polyelectrolytes

Mark J. Stevens and Kurt Kremer
Institut für Festkörperforschung, Forschungszentrum Jülich, Postfach 1913, D-52425 Jülich, Federal Republic of Germany

(Received 15 December 1992)

The level of understanding of charged polymer chains is far less than that of neutral chains. Since they pose difficult theoretical and experimental tasks, they especially warrant simulation studies. We performed molecular dynamics simulations on multichain systems of flexible chains with full Coulomb interactions of monomers and counterions treated explicitly. This model produces osmotic pressure data that agree excellently to experiments and extend them. The chain conformation changes from stretched to coiled as the density increases to semidilute. The persistence lengths show discrepancies with the Odijk *et al.* wormlike chain picture.

PACS numbers: 61.25.Hq, 36.20.–r, 87.15.–v

Polyelectrolytes remain one of the least understood states of condensed matter [1–3]. This is in great contrast to the well developed theory of neutral polymer solutions [4]. Experimentally bulk properties such as viscosity [5] and the osmotic pressure [2] are well established. Yet an understanding of the origin is lacking. This ignorance about the microscopic nature of polyelectrolytes is especially critical since charged polymers are of fundamental importance to biology (e.g., DNA, RNA), to technical applications of water soluble polymers, and to research on their viscoelastic properties. Progress is inhibited by the difficulties encountered in the presence of charges on the polymer chain and the companion counterions. The main complication is the long range nature of the Coulomb interaction which simply cannot presently be handled theoretically without severe approximations. Furthermore, not only does the Coulomb interaction add a new length scale to those of a neutral system, but also the presence of counterions required by charge neutrality adds more length scales. Scaling theories, so useful in neutral polymer theory, are no longer as simple and clearly applicable to polyelectrolytes. Because theoretical and experimental efforts on charged polymers are so difficult, simulation studies are especially warranted.

In this Letter, we describe results of molecular dynamics simulations on salt-free systems of polyelectrolytes that cover the concentration range from dilute to semidilute. We use the freely jointed bead-chain polymer model which has been very successful in simulations of neutral polymers [6]. The system is composed of the charged monomers and the counterions. The charged particles interact via the full Coulomb potential. The solvent is replaced by a dielectric background. This is the simplest model that explicitly handles the counterions. Our work goes beyond previous simulations which only considered a single chain [7,8].

The present understanding of polyelectrolyte structure comes from the limiting case of dilute concentrations where the chain is assumed to take on a simple rod geometry [9–12]. Some work has been done on perturbation of the rod state due to increasing the polymer concentration or adding salt in order to screen the Coulomb interactions [10–14]. These works describe the polymer as a wormlike chain with a persistence length, $L_p = L_e + L_i$, where L_i is the intrinsic persistence length of the uncharged polymer and L_e is the electrostatic persistence length given asymptotically by [10,12]

$$L_e = \Lambda^2 \lambda_B / 4b^2, \tag{1}$$

where the Debye length $\Lambda = \kappa^{-1} = (4\pi\lambda_B\rho_m)^{-1/2}$, the Bjerrum length $\lambda_B = e^2/\varepsilon k_B T$, ε is the dielectric constant of the solution, ρ_m is the monomer density, and b is the distance between charges along the polymer backbone. This form is supposed to hold for $\kappa L > 1$, where L is the contour length of the chain.

The polymer structure in the crossover region between rodlike and coiled conformations is still unclear [1,3,15–17]. Odijk [17] and Hayter *et al.* [1] have proposed similar pictures of polyelectrolyte structure albeit for different physical reasons. Using this picture Odijk has proposed a scaling theory [17]. The chains remain stiff with increasing concentration until $L_e \approx L$ at monomer concentration $c_1^* = 1/16\pi b^2 L$ for $\kappa L > 1$. Above c_1^*, the chains have a wormlike conformation. A second transition occurs at $c_2^* = 0.04/4\pi\lambda_B^3 = 0.003\sigma^{-3}$ when the strand-strand distance ξ equals L_e. It should be mentioned that $\xi < L_e$ is possible in all density regimes. Since this theory is a single chain theory, both densities are not directly connected to the classical chain overlap concentration $c^* = (L/b)/(\pi R^3/6)$, where R is the average end-to-end distance. de Gennes *et al.* [16] have described an alternative picture in the semidilute regime. Instead of the persistence length varying with density, it is pinned at the strand-strand distance. One part of the motivation of the present study is to shed some light on these concentration effects.

Our simulations extend the work of neutral good solvent polymer simulations to polyelectrolytes. Although experiments are often in poor solvent, we use a good solvent, in order to have a well known reference state and in order to compare with similar theoretical work. The difference would only show up in a regime where the

0031-9007/93/71(14)/2228(4)$06.00

electrostatic repulsion becomes less important. Since in the neutral polymer simulations 16 bead chains are sufficiently long, our polyelectrolyte simulations were done with 16, 32, and 64 bead chains. In some cases we extended the runs to $N_b = 128$ beads. The number of chains was either 8 or 16. The bond potential is the standard FENE (finite extendable nonlinear elastic) potential with spring constant $k = 7\epsilon/\sigma^2$, and maximum extent, $R_0 = 2\sigma$, where here, as throughout this Letter, Lennard-Jones units are used [6]. The average bond length is 1.1σ. Excluded volume effects among the monomers and counterions are included via a repulsive Lennard-Jones (RLJ) potential with the cutoff at $2^{1/6}\sigma$ except for the counterion-counterion RLJ interactions which have the cutoff at $2^{1/6}\sigma/4$. In this way counterions cannot get in between neighboring monomers on a chain and are smaller than these monomers.

In contrast to previous simulations we evaluate the Coulomb interaction by a spherical approximation to the Ewald sum given by Adams and Dubey [18]. This involves using a truncated octahedral simulation cell, the Wigner-Seitz cell of a bcc crystal, since it improves the convergence over the simple cubic cell. This method improves upon the minimum image evaluation of Coulomb interactions by an order of magnitude in the energy. The Coulomb coupling strength is determined by the Bjerrum length λ_B, which for this work is taken to be 1σ. The Coulomb pair energies are then weaker than k_BT and the spherical approximation should be sufficient, yet Coulomb systems are notorious for requiring treatment of the long-range interactions beyond the simulation cell. For this reason, we have checked that the results of the approximate form are consistent with the Ewald sum. For our parameters the Manning ratio $\lambda_B/b = 0.9$. Thus, we are slightly below the Manning condensation limit and in the strong interaction regime. These parameters were chosen because many theoretical calculations and experiments have been performed in this crucial regime [1,3,16].

The dynamics of the system is done at constant temperature, $T = 1.2\epsilon$, using the Langevin thermostat with damping constant $\Gamma = 1\tau^{-1}$, and time step 0.015τ [6]. The thermostat incorporates the damping effects stabilizing the system. The motion damping by a real solvent would be much stronger [6]. The length of the simulation is such that the chains move at least 10 times the contour length L. For 32 bead chains this required about 600 000 time steps.

One quantity which is experimentally measured relatively easily and is thus a good test of the simulations is the osmotic pressure Π. The osmotic pressure has been measured on several systems and two scaling regimes are exhibited [2]. At low densities, $\Pi \sim \rho_m^{9/8}$, which is the dependence predicted by Odijk's scaling theory [17]. In the high concentration regime the scaling exponent changes to 9/4, which is the scaling for semidilute neutral polymers [4]. These results suggest that the polyelectrolyte chains are stretched at dilute concentrations and are similar to neutral chains in good solvents at semidilute concentrations. According to Odijk, the crossover should occur at c_2^*, independent of L.

Indeed our simulation results shown in Fig. 1 give two scaling regimes. In the semidilute regime we find the same scaling exponent 9/4. In the dilute regime our results lie slightly higher than Odijk's prediction which the figure shows to become a poor fit at extremely low densities. Fitting the 64 bead data over the smaller experimental density range [2] yields an exponent of 1.05. This is consistent with the experimental osmotic pressure which shows a weak molecular weight dependence in the dilute regime. This is possibly related to the importance of the chain ends as a function of the screening. We also observe a weak chain length dependence, which seems to decrease at low density. For $\rho_m \to 0$ the data agree very well with the expected noninteracting limit, $\Pi = k_BT\rho_m(1+1/N_b)$. The prefactor for Π is very near to 1 as expected, since the density is measured for simulations by the number density.

One striking aspect of the osmotic pressure data is the lack of any chain length dependence of the crossover density, $\rho_m^{(\Pi)} = 0.07 \pm 0.04$, about a factor of 23 larger than the prediction of Odijk. The fact that for $\rho_m > \rho_m^{(\Pi)}$ the Π dependence is that of neutral polymers suggests that the Coulomb interactions are completely screened at $\rho_m = \rho_m^{(\Pi)}$. For complete screening, the Debye screening length should be less than all interparticle distances. The monomer separation is the shortest particle separation

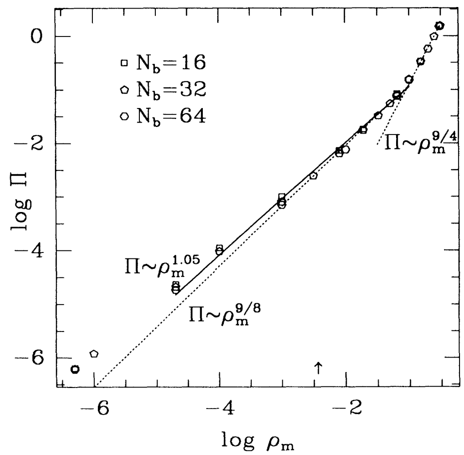

FIG. 1. The osmotic pressure is plotted as a function of the monomer density on a log-log scale for various chain lengths. The 16, 32, and 64 bead chains are represented by squares, pentagons, and hexagons, respectively. For low densities in the experimental range, the pressure scales with an exponent 1.05, slightly below the Odijk prediction marked with an arrow. At high densities the exponent is 9/4, which is that of neutral chains. The errors are smaller than the points. The data show a very weak chain length dependence as in the experimental studies [2].

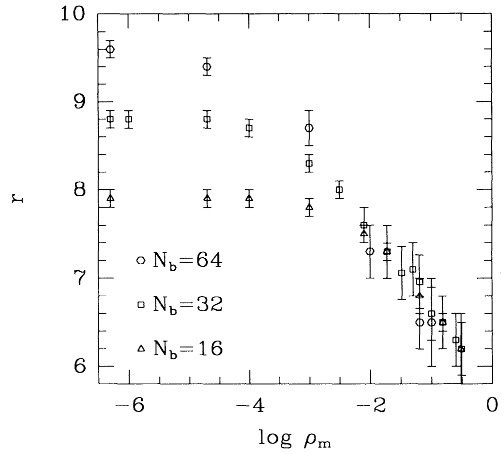

FIG. 2. The ratio of the end-to-end distance and the radius of gyration is plotted versus the log of the monomer density. A value of 12 corresponds to a rigid rod and a value of 6 corresponds to a neutral chain in dense solution (random walk). The dilute-semidilute crossover does not lead to an observable effect in this plot. The densities can be estimated [19] to be $\rho_m \approx 0.20\sigma^{-3}, 0.05\sigma^{-3}$, and $0.017\sigma^{-3}$ for $N = 16, 32$, and 64.

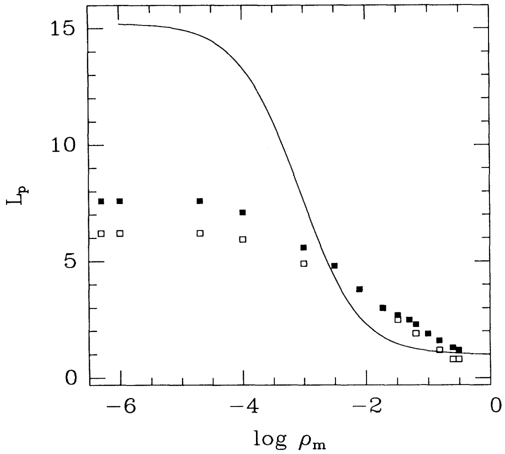

FIG. 3. The persistence length for $N_b = 32$ calculated assuming a wormlike chain (open points) and using the microscopic definition (solid points). The disagreement between the two confirms that the chains are not wormlike. The line gives L_p from Odijk's complete expression including finite size corrections.

distance. We find $\Lambda = b$ at $\rho_m = 1/4\pi\lambda_B b^2 = 0.066\sigma^{-3}$ for our set of parameters. This value agrees perfectly well with our simulation data. It is striking to mention that this density is well above the strand overlap density for $N_b = 64$ while it is still weakly below for $N_b = 16$.

A convenient quantity to analyze the transition from stretched to coiled conformation is the ratio of the average square end-to-end distance and radius of gyration, $r \equiv \langle R^2\rangle/\langle R_G^2\rangle$. For thin rigid rods, $r = 12$; for flexible chains in good solvent, $r \approx 6.3$; for ideal chains, $r = 6$. The plot of r versus ρ_m (Fig. 2) at the highest density is within error approaching the ideal chain value as expected for dense solutions. Although the chains are strongly overlapping, r starts to increase monotonically with decreasing density. The initial increase in r appears to follow a chain length independent curve. Thus, it should also be valid for longer chains. At the lowest densities, there is a chain length dependent saturation such that in the dilute limit the rigid rod value is not reached for any of our chain lengths (see also Fig. 3 below). Longer chains which have more charges have a larger tension and thus are straighter with larger r values. Even in the dilute limit some flexibility persists, resulting in a saturation of r below $r = 12$.

The saturation of r occurs at $\rho_m \simeq 1 \times 10^{-4}\sigma^{-3}$ and $2 \times 10^{-5}\sigma^{-3}$ for $N_b = 16$ and 32, respectively. The $N_b = 64$ case appears to saturate at $1 \times 10^{-6}\sigma^{-3}$. From Odijk's theory one expects a saturation to occur at c_1^*. Because of finite chain length corrections, c_1^* is not defined for these short chain lengths [10]. However, for $N_b = 128$, $c_1^*(N_b)$ is defined and gives $2.8 \times 10^{-5}\sigma^{-3}$. This value is by far too high as it corresponds to the $N_b = 32$ saturation density. Thus the chains do not reach full stretching and continue to increase L_p far below the predicted c_1^* value. One reasonable guess for an alternative calculation of the saturation density, c_1^*, is the density at which there is one counterion per polymer volume, $\rho_m^{(1)} = 1/(\pi R^3/6)$. For densities below this value, the counterions have negligible screening of the intrachain interactions and one expects r to be constant. For N_b =16, 32, and 64, $\rho_m^{(1)} = 2.3 \times 10^{-3}\sigma^{-3}, 2.3 \times 10^{-4}\sigma^{-3}$, and $2.3 \times 10^{-5}\sigma^{-3}$, respectively. These values, and more importantly their ratios, agree much better with our data. Another important point is that the simulation saturation densities are below the overlap densities (see Fig. 2). This result contradicts the de Gennes *et al.* prediction for c_1 [16].

Even though the chains are stretched, the manner of stretching appears to be very different from theoretical expectations. To consider the dilute regime further, we can calculate the persistence length and compare directly to the predictions of theory. The persistence length can be "microscopically" calculated as from [4,7]

$$L_p = \frac{1}{2}\sum_{i=1}^{N_b/2-1} \langle \mathbf{b}_0 \cdot \mathbf{b}_j + \mathbf{b}_0 \cdot \mathbf{b}_{-j}\rangle, \tag{2}$$

where $\mathbf{b}_0 = \mathbf{r}_{N_h} - \mathbf{r}_{N_h+1}$ and $\mathbf{b}_j = \mathbf{r}_{N_h+j} - \mathbf{r}_{N_h+j+1}$ with $N_h = N_b/2$, where $\mathbf{r}_i$ is the position of the ith monomer. Alternatively, similar to experiment, we can calculate the persistence length from the expression for the average end-to-end distance of a wormlike chain:

$$R^2 = 2LL_p - 2L_p^2[1 - \exp(-L/L_p)]. \tag{3}$$

The values of L_p for $N_b = 32$ for the two different methods are plotted in Fig. 3. The error in L_p using either

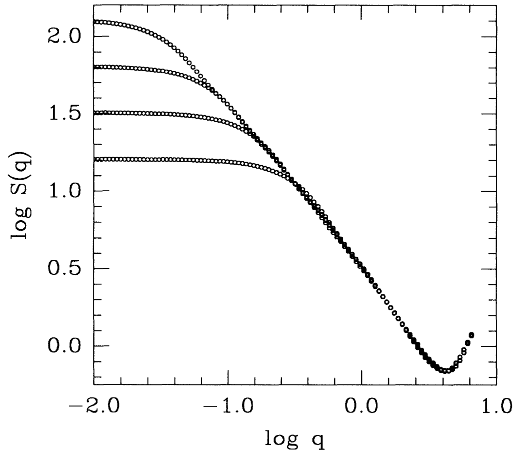

FIG. 4. The form factors for N_b=16, 32, 64, and 128 at $\rho_m = 5 \times 10^{-7}\sigma^{-3}$. These $S(q)$ are independent of chain length for $q > 2\pi/R$.

method is $\pm 0.1\sigma$. Clearly, the two methods do not agree, implying that the chains are not wormlike. The form of the curves is similar to that seen for r with saturation occurring in the extreme dilute limit. We have included Odijk's full expression including finite size effects in Fig. 3. Clearly, our results do not agree with this theoretical curve.

To consider the question of chain length dependence, we examine the form factor, $S(q)$, as a function of N_b. We have calculated $S(q)$ for all densities and find that for $q > 2\pi/R$, there is *no* chain length dependence. For example, Fig. 4 shows $S(q)$ at $\rho_m = 5 \times 10^{-7}\sigma^{-3}$. The shortest chain length, $N_b = 16$, has $R = 9.4\sigma$ and there is a drift away from the longer chain $S(q)$ at $q = 0.6 = 2\pi/R$. Given this chain length independence, we know from the $N_b = 64$ data what the structure is for longer chains for length scales up to 20σ. This again supports the general validity of the present simulations.

The results of these simulations imply a different structure of linear polyelectrolytes than has previously been thought. While the chains are stretched beyond the good solvent structure, they do not attain a fully extended rod conformation. Expecially at the overlap concentration the chains are already significantly contracted in contrast to the picture of de Gennes *et al.* [16]. Moreover, the chain structure is not wormlike, and the density dependence does not conform to the Odijk persistence length calculations. On the other hand, at densities where the Coulomb interactions become strongly screened out, the chains do behave like neutral chains and scaling predictions do agree with our values, though R remains significantly larger than the neutral case.

We would like to acknowledge fruitful discussions with P. A. Pincus and a large grant of computer time from the Höchstleistungsrechenzentrum, Germany within the Disordered Polymers Project. A NATO Travel Grant is gratefully acknowledged.

[1] J. Hayter, G. Janninck, F. Brochard-Wyart, and P.G. de Gennes, J. Phys. (Paris), Lett. **41**, 451 (1980).
[2] L. Wang and V.A. Bloomfield, Macromolecules **23**, 804 (1990).
[3] T.A. Witten and P. Pincus, Europhys. Lett. **3**, 315 (1987).
[4] P.G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1979).
[5] M.W. Kim and D.G. Peiffer, Europhys. Lett. **5**, 321 (1988).
[6] B. Dünweg and K. Kremer, Phys. Rev. Lett. **66**, 2996 (1991); (to be published); K. Kremer and G.S. Grest, J. Chem. Phys. **92**, 5057 (1990).
[7] S.L. Carnie, G.A. Christos, and T.P. Creamer, J. Chem. Phys. **89**, 6484 (1988).
[8] C.E. Reed and W.F. Reed, J. Chem. Phys. **94**, 8479 (1991), and references therein.
[9] G.S. Manning, Quart. Rev. Biophys. **11**, 179 (1978).
[10] T. Odijk, J. Polym. Sci. Polym. Phys. Ed. **15**, 477 (1977).
[11] T. Odijk and A.C. Houwaart, J. Polym. Sci. Polym. Phys. Ed. **16**, 627 (1978).
[12] J. Skolnick and M. Fixman, Macromolecules **10**, 944 (1977).
[13] M. Fixman, J. Chem. Phys. **76**, 6346 (1982).
[14] M. Le Bret, J. Chem. Phys. **76**, 6242 (1982).
[15] M. Cates, J. Phys. II (France) **2**, 1109 (1992).
[16] P.G. de Gennes, P. Pincus, R.M. Velasco, and F. Brochard J. Phys. (Paris) **37**, 1461 (1976).
[17] T. Odijk, Macromolecules **12**, 688 (1979).
[18] D.J. Adams and G.S. Dubey, J. Comput. Phys. **72**, 156 (1987).
[19] K. Kremer, M. J. Stevens, and P. A. Pincus (to be published).