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Monte Carlo studies of the temperature-dependent size of polyelectrolyte chains

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We have performed off-lattice Monte Carlo simulations of isolated, short ($N=40$), fully ionized polyelectrolytes in the presence of a low molecular mass, monovalent salt in the concentration range $0.0 \leq C \leq 1.0$ mol dm^{-3}. The polyelectrolyte is modeled as a freely jointed chain of N hard spherical beads of radius $a=2.0$ Å. The mean-square end-to-end distance and the radius of gyration have been calculated as functions of the Bjerrum length Λ, where $\Lambda = e^2/\varepsilon_0\varepsilon_r kT$. $1/\Lambda$ is thus proportional to the temperature. The results show an interesting temperature dependence; at high temperatures the polyion size decreases with increasing temperature, which is to be expected from simple considerations of the energy/entropy balance. On lowering the temperature, however, we have found that the polyion reaches a maximum size at a certain temperature, which depends on the salt concentration. Further cooling then results in a contraction of the chain. For low salt concentrations, the maximum size represents a rodlike configuration, and the polymer shows a coil-to-rod-to-coil transition as the temperature is increased. We suggest that this behavior is due to the increased screening at low temperatures. The Debye-Hückel approximation does not take into account the fact that for $\Lambda/2a > 1$ Manning condensation will reduce the effective charge of the chain. We have therefore also incorporated this phenomenon into the model in an *ad hoc* fashion by reducing the charge of each band according to the Manning fraction.

I. INTRODUCTION

A fascinating and early recognized aspect of polymer science in general is the high degree to which universal features of polymeric materials can be understood in terms of the large scale structure of the single polymer, without referring to the detailed properties of the particular repeat unit building up the polymer. This property, which applies also to polymers with ionic groups, allows for the use of simple models in both simulations and analytical work. In later years, Monte Carlo simulations have been widely used to study the conformational properties of polyelectrolytes. It is however only recently that the temperature dependence has attracted attention.[1-3] In a recent paper we have studied the temperature dependence of a simplified model in the presence of counterions and no added salt. The Coulomb interaction was fully taken into account. In this work, we perform Monte Carlo simulations of the temperature-dependent conformation of fully ionized macromolecules with added salt in the Debye-Hückel approximation.

II. MODEL AND SIMULATION TECHNIQUE

As was pointed out in the introduction, we are primarily interested in the gross structure of the polyion, which is largely independent of the details of the properties of its constituents. We have thus chosen to disregard such features as fixed carbon-carbon bond angles and hindered rotation potentials and adopted a "minimal model." The polyelectrolyte is modeled as an ordered sequence of $N=40$ spheres (or beads) of radius $a=2.0$ Å, distributed in space under the constraint that the distance between two spheres is greater than or equal to the diameter of the spheres. For two consecutive beads, the distance is equal to the diameter. The beads, which represent the repeat units of the polymer, interact repulsively via a Debye-Hückel potential

$$u_{ij} = \frac{e^2}{\varepsilon_0 \varepsilon_r r_{ij}(1+\kappa a)} \exp[-\kappa(r_{ij}-a)] , \tag{1}$$

where e, ε_0, ε_r, and r_{ij} are the fundamental charge, the vacuum permittivity, the dielectric constant of the solvent, and the distance between beads i and j, respectively. κ is the Debye-Hückel screening parameter

$$\kappa^2 = \frac{8\pi e^2 C}{\varepsilon_0 \varepsilon_r kT} , \tag{2}$$

and C, k, and T are the concentration of simple salt, Boltzmann constant, and absolute temperature, respectively. This corresponds to a chain of N beads of equal charge e immersed in a continuous solvent represented, in the simplest possible way, through its dielectric constant ε_r. The interaction described by Eq. (1) represents the mean-field treatment of the screening due to the presence of mobile monovalent salt ions developed by Debye and Hückel.[4]

The system is taken to be a polyion at infinite dilution, which is apparent from Eq. (2), the counterions do not contribute to the screening but are assumed to be diluted away in this expression. The choice of a Debye-Hückel form of the mean-field potential neglects the attraction of counterions towards the polyion. This well-known phenomenon of counterion condensation[5-10] thus has to be taken into account separately.

A discussion of Manning condensation is easiest to perform in terms of the so-called Bjerrum length Λ:

$$\Lambda = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r kT} . \tag{3}$$

Λ can be interpreted as the distance between two elementary charges for which the potential energy equals the

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thermal energy kT. For water at room temperature, $\varepsilon_r = 78.5$ and $\Lambda = 7.14$ Å. Manning introduced the dimensionless charge density parameter ξ given by

$$\xi = \frac{\Lambda}{b} , \tag{4}$$

where b is the average contour distance between unit charges on the polymer, and showed that for an infinite, cylindrical charge distribution, there exists a critical value of ξ,

$$\xi = 1$$

such that for values of charge density, dielectric constant or temperature leading to

$$\xi > 1$$

counterions will condense on the polyion and reduce the effective charge-density parameter ξ^* to

$$\xi^* = 1 .$$

We have chosen to incorporate Manning condensation into our model in the simplest possible *ad hoc* fashion. For values of Λ such that $\xi > 1$ we have reduced the effective charge of each bead with the condensed fraction

$$F = 1 - \xi^{-1}$$

prescribed by Manning theory. The interaction given by Eq. (1) between the beads is then reduced to an effective interaction

$$u_{ij}^* = \frac{(e/\xi)^2}{\varepsilon_0 \varepsilon_r r_{ij}(1+\kappa a)} \exp[-\kappa(r_{ij} - a)], \quad \xi \geq 1 . \tag{1'}$$

For $\Lambda > 4.0$ Å, we present the results of simulations with and without Manning condensation taken into account.

The Monte Carlo simulations have been performed in the canonical ensemble according to the importance sampling method developed by Metropolis *et al.*[11] A new configuration is generated from the previous and the energy difference is calculated. If the new configuration is a state of lower energy, the change is accepted and the values of the quantities of interest in the new configuration are included in the averages. If the new configuration is one of higher energy, the new state is accepted with probability $P = \exp(-\Delta E/kT)$, averages are collected and the process repeated.

In this work we have adopted a common algorithm for obtaining a new configuration from the previous one. In this algorithm, one end of the chain is selected, at random, to be the head, and the other end to be the tail. The outermost bead at the tail is then removed and a new bead is attached to the head in a random direction but satisfying the requirements of bondlength and nonoverlapping beads.

For each value of C, simulations were performed for a series of values of Λ, starting with the lowest ($\Lambda = 0.0001$) corresponding to the highest temperature. This initial configuration was chosen at random, but for the subsequent values of Λ, the initial configuration was chosen to be the last one of the preceding temperature. For each temperature (or value of Λ), 1 250 000 configurations were generated. The first 250 000 configurations at each temperature were disregarded as atypical and averages were collected from the remaining 1 000 000 configurations.

Program verification was carried out by changing the bondlength to 2.52 Å and fixing the bond angle to $\theta = 109.5$ and comparing the results obtained for various salt concentrations with those obtained for the free rotation model by Carnie, Christos, and Creamer[12] at room temperature. Our results were in all cases within the limits of error stated.

III. RESULTS AND ANALYSIS

We have performed calculations for four different salt concentrations $C = 0.00$, 0.01, 0.10, and 1.00 M. In the following, the model with (without) Manning condensation taken into account will be referred to as DHM [bead-bead interaction is give by Eq. (1′)] and DH, [bead-bead interaction is given by Eq. (1)], respectively. In all figures, the DH model is represented by filled symbols and the DHM model by open symbols. It should be clear from the analysis of the previous section that the two models coincide for $\Lambda \leq 4$ Å. We have calculated the mean-square end-to-end distance $\langle R^2 \rangle$ of the polymer and the mean-square radius of gyration $\langle S^2 \rangle$ where

$$\langle R^2 \rangle = \langle (\bar{R}_1 - \bar{R}_N)^2 \rangle$$

and

$$\langle S^2 \rangle = \frac{1}{N} \sum_{n=1}^{N} \langle (\bar{R}_n - \bar{R}_{\text{CM}})^2 \rangle .$$

R_n is the position vector of the nth bead and R_{CM} is the position of the center of mass of the polymer.

Figure 1 is a plot of the mean-square radius of gyration $\langle S^2 \rangle$ versus $1/\Lambda$ for various concentrations of added salt. The filled symbols show that in the DH model, the size of the polymer increases as the temperature is decreased, until it reaches a maximum. For all but the unscreened case, ($C = 0.00$ M) the polymer then shrinks again and regains its high-temperature value.

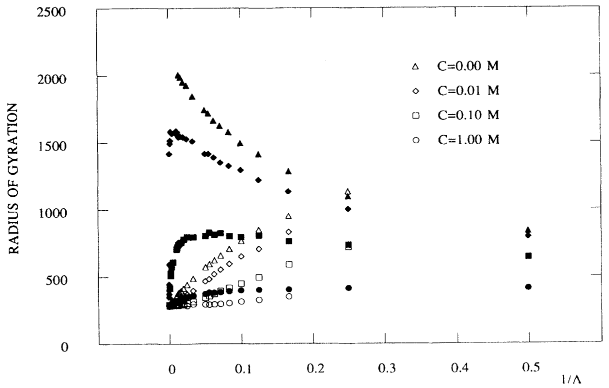

FIG. 1. A plot of the mean-square radius of gyration $\langle S^2 \rangle$ (Å^2) versus $1/\Lambda$ (Å^{-1}) for various salt concentrations. Open (filled) symbols represent simulations with (without) Manning condensation explicitly taken into account.

For low values of salt concentration, the maximum size configuration represents the almost fully stretched polymer and is followed by an abrupt collapse on cooling. For higher salt concentrations, the behavior is not quite as dramatic and the maximum occurs at higher temperatures. The open symbols show the results for the DHM model. We find that the thermal maximum now occurs at the critical temperature $\Lambda=2a$ independent of salt concentration and the configurations are also far from the fully extended conformation for all temperatures and salt concentrations.

These results are further accentuated by Fig. 2. Figure 2 shows the ratio $\langle S^2\rangle/\langle R^2\rangle$ as a function of $1/\Lambda$. It is well known that for ideal chains, the coil configuration corresponds to the ratio $\langle S^2\rangle/\langle R^2\rangle=1/6$.[13] For noninteracting chains of hard spheres, $\langle S^2\rangle/\langle R^2\rangle$ should be slightly larger. It can also be shown that the rodlike conformation is represented by $\langle S^2\rangle/\langle R^2\rangle=1/12$. Figure 2 thus shows that in the DH model, the unscreened chain undergoes a coil-to-rod transition as the temperature is lowered. For $C=0.01$ M we find a similar behavior until we reach very low temperatures when the polymer suddenly collapses. At all higher salt concentrations however, the quota $\langle S^2\rangle/\langle R^2\rangle$ has a minimum far from the rod limit. For the DHM model, Fig. 2 shows that the chains are far from the rod shape at all values of C and Λ. The arrow at the right-hand side of Fig. 2 indicates the high-temperature limit of $\langle S^2\rangle/\langle R^2\rangle$. It is thus observed that the results at high and low temperatures coincide.

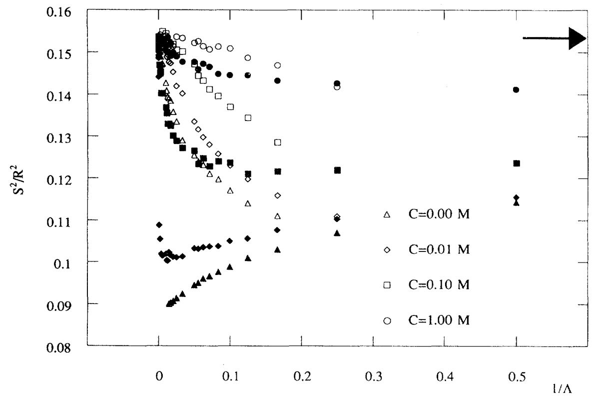

FIG. 2. A plot of the quota $\langle S^2\rangle/\langle R^2\rangle$ versus $1/\Lambda$ (Å^{-1}) for various salt concentrations. Open (filled) symbols represent simulations with (without) Manning condensation explicitly taken into account. The arrow on the right-hand side indicates the high-temperature limit of $\langle S^2\rangle/\langle R^2\rangle$.

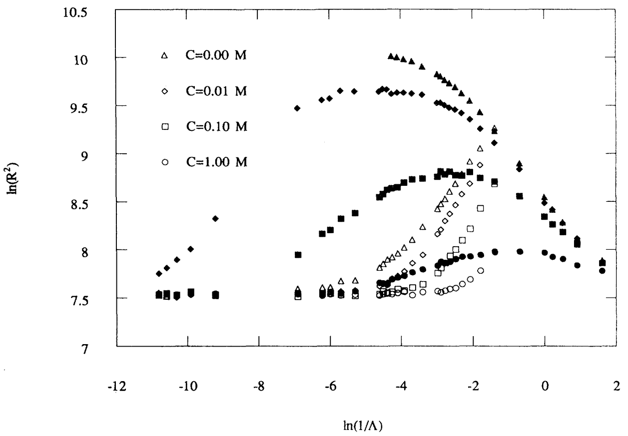

FIG. 3. A plot of $\ln(\langle R^2\rangle)$ versus $1/\Lambda$ (Å^{-1}) for various salt concentrations. Open (filled) symbols represent simulations with (without) Manning condensation explicitly taken into account.

Figure 3 shows an interesting plot of the $\ln(\langle R^2\rangle)$ versus $\ln(1/\Lambda)$. The straight line portions of the curves can be analyzed in terms of scaling arguments showing that, in the DHM model, the slope on the low-temperature side of $\Lambda=4.0$ Å should equal the negative of the slope on the high-temperature side for the case of naked Coulomb interaction. This can best be understood by the following argument. Neglecting the contribution to the excluded volume due to the fact that the beads are not allowed to overlap, the free energy of the polymer consists of the Coulomb energy part and the entropy part. Assuming that the energy E_{el} can be written as a function of R and the square of the total charge Q^2 we have

$$F=E_{\mathrm{el}}(Q^2,R)-TS(R),\quad E_{\mathrm{el}}(Q^2,R)=Q^2 f(R)\,,$$

where $S(R)$ is the entropy. The thermodynamical average of the end-to-end distance should be such that the free energy is a minimum, which leads to a condition $g(R)=Q^2/T$, where $g(R)$ is some function depending on the exact from of $f(R)$ and $S(R)$:

$$g(R)=\frac{\partial S}{\partial R}\left[\frac{\partial f}{\partial R}\right]^{-1}.$$

Since, below the critical temperature, Q is proportional to T, we obtain

$$R=\begin{cases} g^{-1}\left[\dfrac{Q^2}{T}\right], & \Lambda<2a \\ g^{-1}(T), & \Lambda>2a. \end{cases}$$

While it is certainly nontrivial to calculate the exact form of $g(R)$, we thus see that if $g(R)\propto R^{\alpha}$ in the vicinity of the critical value of Λ, we expect a linear dependence of the type shown in Fig. 3. In particular, it follows that the slope for $\Lambda>2a$ should equal the negative of the slope for $\Lambda<2a$ as is observed.

Finally, it is important to discuss the validity of the Debye-Hückel approximation, especially at low temperatures. Actually, in the DH model, for all salt concentrations below 1.0 M, the maximum size of the polymer occurs at a temperature such that $u_{ij}/kT\gg 1$ at the distance of closest approach. There is therefore no *a priori* reason to believe that the Debye-Hückel approximation is useful in these cases. It is instead reasonable to believe that the Debye-Hückel approximation actually underestimates the screening in this regime.[14] Remarkably, however, it has been shown[14] that the Debye-Hückel treatment works for all values of $\xi\leq 1$ in the case of a cylinder-shaped polymer. The assumption underlying this work is that this result also holds for more general conformations. Then, if the temperature is lowered until $\xi > 1$, condensed counterions will reduce the effective value of ξ to $\xi^* = 1$, and the uncondensed charges may still be treated in the Debye-Hückel approximation,[5,7] as is done in the DHM model of this work.

IV. SUMMARY

For the unscreened polyelectrolyte chain without Manning condensation, we find a coil-to-rod transition when the temperature is lowered, in accordance with the results of Brender. Our investigation indicates that inclusion of a small amount of salt ($C < 0.01$ M) does not alter this behavior, except at very low temperatures when increased screening starts to dominate and the polymer retains a coil-like shape. It is then legitimate to talk about a coil-to-rod-to-coil transition. For higher concentrations of added salt (0.01 M $< C <$ 1.00 M) we find that the screening effectively prevents the coil-to-rod transition, and we only observe a smooth variation of the size of the polymer with temperature. The maximum size is lowered with increasing salt concentration and shifted to higher temperatures. Further reducing the interaction by Manning condensation leads to a prevention of the coil-to-rod transition even for the naked Coulomb chain. The relation between the behavior in the DH and DHM models shown in Fig. 3 turned out to be a simple consequence of the way the total charge Q scales with temperature if Manning condensation is taken into account.

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