A computer simulation of charged particles in solution. I. Technique and equilibrium properties*

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A computer technique is presented for simulating the translational motion of ions in a liquid solution. In the model the diffusive motion of each ion is perturbed by the electrostatic force of the surrounding ions. Several polyelectrolyte systems of spherical polyions (10–50 Å in radius) and small ions (1–1 Å in radius) have been studied. For each system the polyion electrostatic shielding length and the average potential energy of each ion species was calculated. When the shielding length was sufficiently short, the computer results and the predictions of the zero polyion concentration Debye–Hückel theory were in good agreement.

I. INTRODUCTION

This paper presents a computer simulation model, originally proposed in a previous work,1 for studying the equilibrium and diffusive properties of charged spherical particles in solution. The model is such that when the particles have zero charge, they independently diffuse through the solution. However, when they are charged, their diffusive motion is perturbed by the electrostatic field of the other ions in the system. The model is applied to dilute polyelectrolyte solutions for the purpose of studying the effects of the polyion–small ion electrostatic interaction. The equilibrium results are presented and shown to be equivalent to those which a Monte Carlo study would yield. In the following article the effect of the polyion–small ion electrostatic interaction upon the polyion diffusion coefficient is studied.2

As a minimum, a polyelectrolyte solution is a three component system. In addition to the solvent molecules and the macroions or polycations which can carry a large number of ionic charges, these solutions must also contain a sufficient number of small counterions, whose charge is of the opposite sign to that of the polyions, to maintain charge neutrality. Often, there are also present small ions whose charge is of the same sign as the polyion charge. These will be called byions. The small ions are generally only singly or doubly ionized and their concentration must be such that the net charge of the system as a whole is zero.

The equilibrium and transport properties of polyelectrolyte solutions are profoundly affected by the electrostatic interactions between the various ions. The equilibrium properties, especially in the case of dilute polyion concentration, have been treated theoretically by applying the Debye–Hückel theory.3–5 In these works expressions for the electrostatic energy of the ions, the electrostatic shielding of the polyions by the small ions, and the colligative properties of the system are developed. When a macroscopic ion concentration gradient is introduced into the system, a macroscopic electrostatic field is produced as each ion species relaxes toward the equilibrium concentration at a different rate. The macroscopic electrostatic field generally tends to decrease the average velocity of the faster ions while increasing that of the slower ions. Problems of this type have been treated by many authors.6–10

In this work the effects of the polyion–small ion electrostatic interaction are studied for systems at thermodynamic equilibrium. Although there is no macroscopic electrostatic field present, as each ion diffuses through the solvent it experiences a fluctuating electrostatic force due to the other ions in the system. Of main interest in this study is the average electrostatic potential energy of each ion species, the electrostatic shielding of the polyions by the small ions, and the effect of the fluctuating electrostatic force upon the polyion diffusion coefficient. In the computer calculations of the polyion motion, the polyion concentration is assumed to be sufficiently dilute so that, along with the shielding of the small ions, the polyion–polyion contribution to the fluctuating electrostatic force can be neglected. However, the polyion–polyion contribution to the polyion potential energy is included.

For one-component systems where the particles interact through an inverse power potential, \( \phi(r) = \alpha/r^s \), the properties of the system can be expressed in terms of the single dimensionless parameter \( \Gamma = (\alpha/kT)^{1/s} \). Here \( \rho \) is the average number density, \( T \) is the absolute temperature, and \( k \) is the Boltzmann constant. This is not possible for the present polyion–small ion model since they are assumed to be hard spheres where each species has a different size, charge, and concentration. In the computer experiments the polyion radius was varied from \( R_p \sim 10–50 \, \text{Å} \), with most of the calculations being carried out with \( R_p \sim 20 \, \text{Å} \). The polyion charge and the small ion charge, mobility, and concentration were also varied.

II. COMPUTER SIMULATION MODEL

The model treated in this study consists of a system of hard sphere polyions and small ions (counterions and byions) in a liquid solvent with a uniform dielectric constant. Each ion has a constant net charge with the polyions having a charge \( -Q \), the counterions a charge \( +q \), and the byions a charge \( -q \). The values of \( q \) and \( Q \) are positive integral multiples of the basic electron charge and the number of counterions and byions per polyion is such that the net charge of the system is always zero. In this model the polyions represent the physical polyelectrolytes in real polyelectrolyte solutions including any bound small ions and solvent molecules. The small ions represent the unbound small ions present in polyelectro-
lytes and, as such, they are always free in the sense of never being bound to the polyions even though many small ion-polyion collisions do occur.

The potential of interaction between two ions is the Coulomb potential for hard spheres

\[ \phi_{ij} = \begin{cases} \frac{q_i q_j}{\epsilon r_{ij}} & r_{ij} > r_0 \\ \infty & r_{ij} < r_0, \end{cases} \]

where \( q_i, q_j \) are the respective charges on the two ions, \( \epsilon \) is the dielectric constant of the solvent, \( r_{ij} \) is the distance between the particles, and \( r_0 \) is the sum of the two ion radii. The force on ion \( i \) due to ion \( j \) is therefore

\[ \mathbf{F}_{ij} = -\nabla_i \phi_{ij} = (q_i q_j / \epsilon r_{ij}^2) \hat{r}_{ij}, \]

where \( \hat{r}_{ij} \) is a unit vector from ion \( j \) to ion \( i \). And the total force on ion \( i \) is given by

\[ \mathbf{F}_i = \sum_{j \neq i} \frac{q_i q_j}{\epsilon r_{ij}^2} \hat{r}_{ij}. \]

The summation extends over all ions in the infinite system except ion \( i \). In order to avoid this infinite summation in the computer calculations and yet still account for the effects of the ion images in cells outside the basic cell, the pair potential and pair force are modified, as shown in the following section.

In order for this simulation to be practical on present day computers, the time step used in calculating the motion of the ions must be much greater than the mean ion collision time.\(^1\) Therefore, it is proposed that during each time step the ions be treated as independently diffusing particles where the motion of each ion is perturbed by the electrostatic interaction with the other ions in the system. Then the motion of each ion can be described by the Smoluchowski equation which is

\[ \frac{\partial P(r)}{\partial t} = D_\theta \nabla^2 P - \frac{D_\theta}{kT} \nabla \cdot (P \mathbf{F}). \]

Here, \( P \) is the probability distribution function which governs the probability that the particular ion of interest will undergo a displacement \( \Delta t \) during the time interval \( \Delta t \). The constant \( D_\theta \) is the zero charge diffusion coefficient for this ion, \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, and \( \mathbf{F} = \mathbf{F}(r, t) \) is the net electrostatic force which the ion experiences due to the other ions in the system. If \( \Delta t \) is sufficiently short so that the fastest ions move only a short distance, then \( \mathbf{F}(r, t) \) is nearly constant during \( \Delta t \) and the solution to Eq. (4) is

\[ P[\mathbf{r} + \Delta \mathbf{r}, \mathbf{F}] = \left( \frac{1}{4\pi D_\theta \Delta t} \right)^{3/2} \exp \left[ -\frac{\mathbf{r}(t + \Delta t) - \mathbf{r}(t) - \frac{D_\theta}{kT} \mathbf{F}(t) \Delta t}{4D_\theta \Delta t} \right]. \]

The mean and mean square displacements are seen to be

\[ \langle \Delta \mathbf{r} \rangle = \frac{D_\theta}{kT} \mathbf{F}(t) \Delta t, \]

\[ \langle \Delta \mathbf{r}^2 \rangle = 6D_\theta \Delta t + \left( \frac{D_\theta \mathbf{F}(t) \Delta t}{kT} \right)^2. \]

The ion equation of motion is therefore

\[ \mathbf{r}(t + \Delta t) = \mathbf{r}(t) + R_s(\Delta t) + \frac{D_\theta}{kT} \mathbf{F}(t) \Delta t, \]

where \( R_s(\Delta t) \) is a random displacement which is governed by a Gaussian probability distribution function with an average value of zero and a mean square value of \( 6D_\theta \Delta t \). Physically, the displacement \( R_s(\Delta t) \) represents the random diffusive displacement which the ion undergoes due to its many collisions with the solvent particles during the time \( \Delta t \), and the displacement \( R_s(\Delta t) = (D_\theta / kT) \mathbf{F}(t) \Delta t \) represents the displacement which the ion undergoes due to the electrostatic force \( \mathbf{F}(t) \) from the other ions in the system. There is no equation for the ion velocity since the time step is so long that nearly all velocity information is lost from one time step to the next. However, the electrostatic force contribution to the velocity autocorrelation function can be obtained from the mean square displacement.\(^2\)

For large particles in the absence of charge effects, the relationship between the particle diffusion coefficient and radius is generally taken to be given by the Stokes–Einstein law

\[ D_\theta = kT / 6\pi \eta R, \]

where \( \eta \) is the shear viscosity of the solvent. However, the situation for the small ions is not so clear.\(^11-15\) Added to the difficulty that the small ions are about the same size as the solvent molecules, the small ions are undoubtedly hydrated so that the observed diffusion coefficients are not those of "bare" ions but of solvated ions. For simplicity, the radius of the small ions will also be specified by the Stokes–Einstein law.

The motion of the individual solvent particles is not calculated. The effects of the solvent particles on the ions are assumed to consist of causing the random displacement \( R_s(\Delta t) \) of each ion and of creating a dielectric constant \( \epsilon \). Thus, the part of the polyion diffusion coefficient which is due to collisions with the solvent particles \( D_\theta \) is assumed and the change due to the polyion-small ion electrostatic interaction can be obtained by subtracting \( D_\theta \) from the calculated total diffusion coefficient.

In the actual computer calculations only a relatively small number of particles can be dealt with; however, in order to reduce surface effects the number of particles must be very large. As a compromise between these two extremes, the system is made to be periodic. That is, the system consists of a number of particles within a basic cubic cell of side length \( L \) which is then periodically repeated throughout three-dimensional position space. The basic cell contains a single polyion and a sufficient number of counterions and byions to maintain charge neutrality with the remainder of the cell filled with solvent particles. Although the electrostatic interaction between ions extends beyond a single cell and must therefore be accounted for, only the ion positions in the basic cell need to be monitored since the system is periodic. If a particle travels out one side of the cell, an image enters the cell through the opposite side so that the number of particles in each cell remains constant.
Notice that the distance between polyions is constant so that the force on a polyion due to the other polyions is always zero. Therefore, the polyion–polyion electrostatic interaction cannot contribute to the polyion diffusion coefficient and any change is due solely to the polyion–small ion electrostatic interaction. On the other hand, the polyion–polyion potential interaction does contribute to the total potential energy of the system.

The procedure to be used in the computer experiments is therefore as follows. The ions are all given an initial position within the solvent. During each time step, each ion undergoes a displacement according to Eq. (8) where the random displacement $\mathbf{R}_i$ is randomly\(^{16}\) chosen from $10^6$ equally probable values taken from a histogram approximation to the continuous Gaussian distribution. The only exception is when one ion is displaced inside of another; then, the ion undergoing the displacement is reflected back outside of the stationary one. As the ions move through the solution in this way, the various parameters of interest are monitored to determine the statistical properties of the system.

III. MODIFIED PAIR POTENTIAL AND PAIR FORCE

The electrostatic potential energy of an ion in the basic cell involves an infinite sum of Coulomb pair potentials over the remaining ions in the basic cell plus all of the images. Since the Coulomb potential is a long range potential, it is generally necessary to include the interactions with the images in order to calculate the potential energy accurately. This presents a great computational problem as the time involved in such calculations would be enormous. However, in a study of a one component plasma, Brush, Sahlin, and Teller presented a method for calculating a modified pair potential which includes the interaction of the images.\(^{17}\) This reduced the infinite summation to a sum over only the remaining ions in the basic cell.

Applying their method to the present system of hard sphere ions in a uniform dielectric solvent, one starts with Poisson’s equation

$$
\nabla^2 \phi(\mathbf{r}) = -(4\pi/\epsilon)\rho(\mathbf{r}),
$$

(10)

where $\phi(\mathbf{r})$ is the potential due to the charge distribution $\rho(\mathbf{r})$ and $\epsilon$ is the dielectric constant of the solution. If the actual charge distribution for the ions was used in Eq. (10), it would be mathematically difficult to solve. However, neglecting the self-energy of the ions, the electrostatic potential energy of a system of spherically symmetric hard ions is the same as that for a system of point charges. Therefore, in calculating the potential energy, the ions can be treated as point charges.

In each cell of the system there is one polyion of charge $-Nq$, $N+M$ counterions of charge $+q$, and $M$ byions of charge $-q$ so that the charge distribution within the basic cell is

$$
\rho(\mathbf{r}) = q \sum_{i=1}^{N+M} a_i \delta(\mathbf{r} - \mathbf{r}_i) - Nq \delta(\mathbf{r}),
$$

(11)

where

$$
a_i = \begin{cases} +1 & \text{for } 1 \leq i \leq N + M \\ -1 & \text{for } N + M + 1 \leq i \leq N + 2M \\ -N & \text{for } i = N + 2M + 1 = N + 2M + 1 
\end{cases}
$$

and $\delta$ is the Dirac delta function. All the ions in the remaining cells can be included in Eq. (11) by expressing $\rho(\mathbf{r})$ in terms of a periodic Fourier series as follows:

$$
\rho(\mathbf{r}) = \frac{1}{V} \sum_{k} \rho_k e^{i\mathbf{k}\cdot\mathbf{r}}, \quad \mathbf{k} = \frac{2\pi}{L} \mathbf{n},
$$

(12)

where $V$ and $L$ are the volume and edge length of the basic cell, and $\mathbf{n}$ is a vector with integer components. Evaluating $\rho_k$, the charge distribution for the infinite system is

$$
\rho(\mathbf{r}) = \sum_{i=1}^{N} a_i \sum_{J} e^{i\mathbf{k}\cdot(\mathbf{r} - \mathbf{r}_i)},
$$

(13)

where the prime on the summation indicates exclusion of the $k=0$ term.

Expressing the potential in terms of a Fourier series

$$
\phi(\mathbf{r}) = \frac{1}{V} \sum_{k} \phi_k e^{i\mathbf{k}\cdot\mathbf{r}}
$$

(14)

substituting Eqs. (13) and (14) into Eq. (10), and then equating coefficients of terms containing the same value of $k$, yields the following expression for the periodic potential:

$$
\phi(\mathbf{r}) = -\frac{4\pi\rho}{\epsilon V} \sum_{i=1}^{N} a_i \sum_{J} \frac{1}{\mathbf{k}^2} e^{i\mathbf{k}\cdot(\mathbf{r} - \mathbf{r}_i)}.
$$

(15)

To obtain the total electrostatic potential energy of the ions in the basic cell one needs to evaluate the expression

$$
U = \left(\frac{1}{2}\right) \int d^3 r \rho(\mathbf{r}) \phi(\mathbf{r}) - \frac{2}{2\epsilon \mathbf{L}} \sum_{i=1}^{N} a_i \int d^3 r \delta(\mathbf{r} - \mathbf{x}_i) \int d^3 r \delta(\mathbf{r} - \mathbf{x}_i),
$$

(16)

where the second term removes the infinite self-energy of the point ions.

After carrying out the integration in Eq. (16), the resultant sum can be expressed in a convenient form by using the lattice summation techniques of Ewald.\(^{18,19}\) Changing from a sum over $k$ to a sum over $n$, $[k = (2\pi/L) \times n]$, and expressing the ion positions as reduced variables so that $x_{ij} = (x_i - x_j)/L$, then the total electrostatic potential energy is

$$
U = \left(\frac{1}{2}\right) \sum_{i=1}^{N} \sum_{j=1}^{N} \psi(x_{ij})
$$

$$
= \left(\frac{1}{2}\right) \sum_{i=1}^{N} \sum_{j=1}^{N} a_i a_j \frac{\epsilon \mathbf{L}}{\mathbf{r}_{ij}} \left[\psi_1(x_{ij}) + \psi_2(x_{ij})\right],
$$

(17)

where

$$
\psi_1(x) = \text{erfc}(x^{1/2}/x) / x - 1 - Em,
$$

$$
\psi_2(x) = \sum_{n} \left[ \frac{\text{erfc}(x^{1/2}/|n - x|) \cdot e^{-x^2 \cos(2\pi n \cdot x)}}{|n - x|^2} \right],
$$

and $Em = 2.83729479$ is the Madelung constant of a simple cubic lattice.\(^{20}\) The modified pair potential is $\psi$ and it is compared with the Coulomb potential in Fig. 1.
The modified pair force is readily obtained from the gradient of the modified pair potential.

In the computer calculations of the modified pair force and potential, the anisotropic terms were approximated by a polynomial expansion of the form used by Hansen in which the first three terms were kept. The spherically symmetric terms were tabulated at 88 points and linearly interpolated for the points between.

IV. EQUILIBRIUM CALCULATIONS

The distance between each small ion and the nearest polyion is tabulated during each time step of the computer experiment. From these data the distribution functions for the counterions \( P_+(r) \), the byions \( P_-(r) \), and the small ion charge \( P(r) \) are made. For a system where each cell contains \( N + M \) counterions and \( M \) byions the small ion charge distribution is defined to be

\[
P(r) = 1/N \sum (N + M) P_j(r) - MP_j(r).
\]  

All three distribution functions are normalized so that the integral of each over the volume of the basic cell is one. An example of these functions is shown in Fig. 2.

The concentration of counterions near a polyion is relatively high since the interaction between them is attractive. On the other hand, the concentration of byions is relatively low near a polyion since the interaction is repulsive. This effect tends to shield the charge of the polyion and the degree of shielding can be seen from the net charge distribution

\[
W(r) = \frac{1}{2} \int_{r_{\text{min}}}^{r} d^3r P(r) \cdot r_{\text{min}} = r_p + r_i;
\]  

where the integral is over the volume of the basic cell from \( r_{\text{min}} \), the minimum distance between a polyion and small ion, to the radius \( r \). The maximum value of \( W \) occurs at the polyion radius where \( W(r_p) = 1 \). Its value decreases monotonically to zero at the maximum radius \( r_{\text{max}} = (3^{1/2}/2)L \). In order to quantitatively measure the shielding effect, the shielding length is arbitrarily defined to be

\[
W(r_p) = 0.1.
\]  

Recalling Eq. (17), the average electrostatic energy per cell is

\[
U = \frac{1}{2} \sum_{i \neq j} \sum_{n} \langle \phi_{ij} \rangle,
\]  

where \( \phi_{ij} \) is the modified pair potential between ions \( i \) and \( j \) in the basic cell. The average electrostatic energy can be separated by species and if this is done one obtains

\[
U = \sum_i U_i; \quad i = p, c, b,
\]  

where

\[
U_p = \frac{1}{2} (N + M) \langle \phi_{pc} \rangle + \frac{M}{2} \langle \phi_{pb} \rangle,
\]

\[
U_c = \frac{1}{2} (N + M) \langle \phi_{cp} \rangle + (N + M - 1) \langle \phi_{cc} \rangle + M \langle \phi_{cb} \rangle,
\]

\[
U_b = \frac{1}{2} M \langle \phi_{pb} \rangle + (N + M) \langle \phi_{cb} \rangle + (M - 1) \langle \phi_{bb} \rangle,
\]

with \( p = \) polyions, \( c = \) counterions, and \( b = \) byions.

In the above discussion, the system of infinitely separated ions is used as the reference with the energy of the system taken to be zero. Another useful reference is the neutral small ion system of \( M \) counterion–byion pairs per cell. The average electrostatic energy of this system can be approximated by

\[
U_{KS} = [(M - 1) \langle \phi_{cc} \rangle + 2M \langle \phi_{cb} \rangle].
\]  

The equilibrium results obtained using the simulation technique presented in Sec. II are equivalent to those

\[
U = \sum_i U_i; \quad i = p, c, b,
\]  

where

\[
U_p = \frac{1}{2} (N + M) \langle \phi_{pc} \rangle + \frac{M}{2} \langle \phi_{pb} \rangle,
\]

\[
U_c = \frac{1}{2} (N + M) \langle \phi_{cp} \rangle + (N + M - 1) \langle \phi_{cc} \rangle + M \langle \phi_{cb} \rangle,
\]

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U_b = \frac{1}{2} M \langle \phi_{pb} \rangle + (N + M) \langle \phi_{cb} \rangle + (M - 1) \langle \phi_{bb} \rangle,
\]

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\]  

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TABLE I. A quantitative description of the basic system.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 polyion per cell of side length, ( L = 202.00 ) Å</td>
<td></td>
</tr>
<tr>
<td>( D_q = 1 \times 10^{-6} ) cm(^2)/sec</td>
<td></td>
</tr>
<tr>
<td>( R_q = 21.43 ) Å</td>
<td></td>
</tr>
<tr>
<td>Volume concentration, ( c = 0.005 )</td>
<td></td>
</tr>
<tr>
<td>( R_{ste} = R_q + R_s = 22.50 ) cm</td>
<td></td>
</tr>
<tr>
<td>( Q = 2Ne )</td>
<td></td>
</tr>
<tr>
<td>( N + M ) counterions per cell</td>
<td></td>
</tr>
<tr>
<td>( D_q = 2 \times 10^{-5} ) cm(^2)/sec</td>
<td></td>
</tr>
<tr>
<td>( R_q = 1.07 ) Å</td>
<td></td>
</tr>
<tr>
<td>( q = 2e )</td>
<td></td>
</tr>
<tr>
<td>( M ) byions per cell</td>
<td></td>
</tr>
<tr>
<td>( D_q = 2 \times 10^{-6} ) cm(^2)/sec</td>
<td></td>
</tr>
<tr>
<td>( R_q = 1.07 ) Å</td>
<td></td>
</tr>
<tr>
<td>( q = -2e )</td>
<td></td>
</tr>
<tr>
<td>Dielectric constant, ( \varepsilon = 78.54 )</td>
<td></td>
</tr>
<tr>
<td>Temperature, ( T = 20 ) °C</td>
<td></td>
</tr>
<tr>
<td>Time step, ( \Delta t = 4 \times 10^{-11} ) sec</td>
<td></td>
</tr>
</tbody>
</table>

which would be obtained from a Monte Carlo simulation\(^{22,23}\) on the same system. This can be seen by returning to Eq. (4) for the single ion distribution function. The steady state distribution function for a single ion with the remaining ions in a fixed configuration is given by

\[
\nabla P = \frac{FP}{kT} = - (\nabla \phi/kT)P
\]

or

\[
P(x) = P_0 \exp\left(-\frac{\phi(x)}{kT}\right),
\]

where \( \phi(x) \) is the ion potential energy at \( x \) and \( P_0 \) is a constant. Thus, the probability of each possible configuration is governed by the Boltzmann distribution law just as it is in a Monte Carlo simulation.

V. EQUILIBRIUM RESULTS

The polyion systems studied in this work were modeled after the globular proteins. These molecules are generally less than 50 Å in radius and their dynamic behavior can be approximated fairly well by that of theoretical spheres.\(^3\) The main system studied is described in Table I. Each cell contains a single polyion which has a zero charge diffusion coefficient of \( 1 \times 10^{-6} \) cm\(^2\)/sec and therefore a radius of 21.43 Å. There are also \( N + M \) counterions and \( M \) byions per cell. The value of \( N \) is varied from 2 to 8 and that of \( M \) from 0 to 24. These small ions have a zero charge diffusion coefficient of \( 2 \times 10^{-5} \) cm\(^2\)/sec with a corresponding radius of 1.07 Å and a charge of \( \pm 2e \). The side length of the basic cell is 202 Å which corresponds to a polyion volume concentration of 0.005. The dielectric constant and temperature of the entire solution are, respectively, 78.54 and 20 °C. Additional computer runs were made in which the polyion size and concentration and the small ion charge and mobility were varied.

The time step used in the equation of motion depended upon the zero charge value of the diffusion coefficients. For the runs with \( D_q = 2 \times 10^{-5} \) cm\(^2\)/sec, a time step of \( \Delta t = 4 \times 10^{-11} \) sec was used. The total number of time steps per run ranged from \( 1.28 \times 10^5 \) to \( 5.12 \times 10^6 \) depending upon the number of small ions. As the number of small ions increased, the total number of steps decreased.

A. Small ion charge distribution functions and shielding length

The small ion charge distribution about a polyion \( P(x) \) is defined by Eq. (19) as the difference between the average counterion and the average byion distributions. Figure 3 shows a composite graph of \( P(x) \) for the basic system described in Table I with no byions present (\( M = 0 \)). For these results, the counterion diffusion coefficient is \( D_q = 2 \times 10^{-5} \) cm\(^2\)/sec; however, except for the change in \( R_{ste} = R_q + R_s \), \( P(x) \) was insensitive to changes in the small ion diffusion coefficient. In the volume close to the polyion, the counterion concentration is seen to increase with polyion charge so that the shielding of the central polyion is more effective at shorter distances. This type of monotonically decreasing function was typical for all the cases considered.

The shielding effects of the small ions are perhaps better visualized from a plot of the net charge distribution \( W(x) \) defined by Eq. (20). \( W(x) \) is proportional to the average net charge interior to \( x \) within the basic cell. In Fig. 4, \( W(x) \) is plotted for the four cases of Fig. 3. The electrostatic shielding at short distances from the central polyion is seen to rapidly increase as the polyion charge increases. The shielding length, given by \( W(x) = 0.1 \), decreases slightly from 0.63 for \( Q = -4e \) to 0.58 for \( Q = -16e \).

Figure 5 shows the effect of adding neutral pairs of small ions upon \( W(x) \). The case is the same as before only the polyion concentration is 0.01 and the polyion charge is held constant at \( Q = -16e \). The constant \( M \) is the number of counterion-byion pairs present in each cell. The shielding length decreases quite significantly with increases in \( M \). For \( M = 0 \), \( r_s = 0.58L \) while for \( M = 24 \), \( r_s = 0.39L \).

The values of the shielding length for all the cases

![Graph](https://example.com/graph.png)
considered are listed in Tables II and III. As the pol­
yion charge increases, the shielding length is seen to
to always decrease slightly. In the absence of byions,
ion-counterion pairs decreased the shielding length
from the cases with the same polyion charge and
additional neutral small ion pairs
of the counterion diffusion coefficient
considered are listed in Tables II and III. As the poly­
ion charge increases, the shielding length is seen to
always decrease slightly. In the absence of byions,
ion-counterion pairs decreased the shielding length
quite rapidly.

**B. Electrostatic energy**

The calculated values of the electrostatic energy for
each ion species are also presented in Tables II and III.
The data in Table II are for the computer runs with no
additional neutral small ion pairs \( M=0 \). In Part A of
Table II the results are given for the basic system de­
scribed in Table I. Within the accuracy of the calcula­
tions, there was no change in the results when the value
of the counterion diffusion coefficient \( D_1 \) was changed to
\( 1 \times 10^{-5} \text{ cm}^2/\text{sec} \), so these results are also presented
here. The potential energy of the system is independent
of the sign of the polyion charge and is therefore seen
to always decrease as the magnitude of the polyion
charge is increased. The dependence on polyion charge is
roughly \( U \propto Q^2 \) for the smaller values. Part A2 of
Table II presents the results for the basic system with
the counterion charge \( q=1e \). The magnitude of the po­
tential energy is reduced by a factor of about \((1/2)^{1/2}\)
from the cases with the same polyion charge and \( q=2e \).
This indicates a potential energy dependence on counter­
ion charge of \( U \propto q^{12} \). The effect of polyion concentration
within the range \( 0.001 \leq c \leq 0.02 \) is shown in Part
A3 of Table II for a polyion charge of \( -12e \). As the
polyion concentration becomes more dilute, the magni­
tude of the potential energy for each ion species de­
creases. This is because the ions spend more time at
greater distances from each other.

In Part B of Table II, the results are given for sys­
tems containing polyions with a zero charge diffusion
coefficient \( D_0 = 2 \times 10^{-4} \text{ cm}^2/\text{sec} \) and \( 0.5 \times 10^{-6} \text{ cm}^2/\text{sec} \) at a 0.01 concentration.
Again, there are no byions present and the qualitative features of these results are the same
as those in the previous case.

### Table II. Electrostatic shielding length and potential energy

<table>
<thead>
<tr>
<th>( -Q/e )</th>
<th>( r_f/L )</th>
<th>( r_s )</th>
<th>( U_p )</th>
<th>( U_c )</th>
<th>( U )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.63</td>
<td>127</td>
<td>-0.35</td>
<td>-0.20</td>
<td>-0.55</td>
</tr>
<tr>
<td>8</td>
<td>0.61</td>
<td>124</td>
<td>-1.62</td>
<td>-0.65</td>
<td>-2.27</td>
</tr>
<tr>
<td>12</td>
<td>0.60</td>
<td>121</td>
<td>-4.15</td>
<td>-1.69</td>
<td>-5.75</td>
</tr>
<tr>
<td>16</td>
<td>0.58</td>
<td>118</td>
<td>-8.30</td>
<td>-3.20</td>
<td>-11.5</td>
</tr>
</tbody>
</table>

1. \( D_1 = 1 \times 10^{-4} \text{ cm}^2/\text{sec} \), \( R_0 = 21.43 \text{ Å} \), \( c = 0.005 \text{ (L = 202 Å)} \)
2. \( D_1 = 2 \times 10^{-4} \text{ cm}^2/\text{sec} \), \( q = 2e \)

Part B is for systems containing polyions with a zero
charge diffusion coefficient \( D_0 = 2 \times 10^{-4} \text{ cm}^2/\text{sec} \) and \( q = 6e \) also at 0.01 concentration.

### Table III.

<table>
<thead>
<tr>
<th>( -Q/e )</th>
<th>( r_f/L )</th>
<th>( r_s )</th>
<th>( U_p )</th>
<th>( U_c )</th>
<th>( U )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.68</td>
<td>50.3</td>
<td>-0.22</td>
<td>-0.22</td>
<td>-0.44</td>
</tr>
<tr>
<td>4</td>
<td>0.61</td>
<td>48.8</td>
<td>-0.58</td>
<td>-0.58</td>
<td>-1.56</td>
</tr>
<tr>
<td>6</td>
<td>0.59</td>
<td>47.3</td>
<td>-2.45</td>
<td>-1.23</td>
<td>-3.67</td>
</tr>
</tbody>
</table>

The statistical fluctuations in the results indicate an error of 1% for the
shielding length and 3% for the potential energy.

Table III summarizes the equilibrium results for the
computer runs with additional neutral small ion pairs
added. Part A is for systems containing polyions with
\( D_0 = 1 \times 10^{-4} \text{ cm}^2/\text{sec} \) and \( Q = 16e \) at a 0.01 concentration and
Part B is for systems containing polyions with \( D_0 =
2 \times 10^{-4} \text{ cm}^2/\text{sec} \) and \( Q = 6e \) also at 0.01 concentration.

The magnitude of the potential energy per cell is seen

![FIG. 4. The net charge distribution function with \( M=0 \). \( (D_0 = 1 \times 10^{-4} \text{ cm}^2/\text{sec} \), \( D_1 = 2 \times 10^{-4} \text{ cm}^2/\text{sec} \), and \( L = 202 \text{ Å} \).](image-url)

![FIG. 5. The net charge distribution function with excess neutral small ion pairs. \( (D_0 = 1 \times 10^{-4} \text{ cm}^2/\text{sec} \), \( D_1 = 2 \times 10^{-4} \text{ cm}^2/\text{sec} \), and \( L = 160.33 \text{ Å} \).](image-url)
TABLE III. Electrostatic shielding length and potential energy II.

<table>
<thead>
<tr>
<th>M</th>
<th>φ</th>
<th>U_p</th>
<th>U</th>
<th>U_{NS}</th>
<th>U - U_{NS}</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>92.4</td>
<td>-9.5</td>
<td>-2.28</td>
<td>-12.8</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>84.4</td>
<td>-10.3</td>
<td>-2.33</td>
<td>-15.5</td>
<td>-1.03</td>
</tr>
<tr>
<td>8</td>
<td>78.4</td>
<td>-10.6</td>
<td>-2.52</td>
<td>-18.4</td>
<td>-2.52</td>
</tr>
<tr>
<td>16</td>
<td>71.7</td>
<td>-11.0</td>
<td>-2.62</td>
<td>-22.4</td>
<td>-5.09</td>
</tr>
<tr>
<td>24</td>
<td>63.1</td>
<td>-11.5</td>
<td>-3.33</td>
<td>-31.0</td>
<td>-11.7</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>47.2</td>
<td>-2.45</td>
<td>-1.23</td>
<td>-2.67</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>42.4</td>
<td>-2.71</td>
<td>-2.35</td>
<td>-6.12</td>
<td>-2.93</td>
</tr>
<tr>
<td>8</td>
<td>39.7</td>
<td>-2.84</td>
<td>-5.25</td>
<td>-15.1</td>
<td>-7.15</td>
</tr>
<tr>
<td>16</td>
<td>332</td>
<td>-3.04</td>
<td>-10.9</td>
<td>-9.73</td>
<td>-23.7</td>
</tr>
<tr>
<td>24</td>
<td>29.6</td>
<td>-3.22</td>
<td>-16.7</td>
<td>-35.5</td>
<td>-28.0</td>
</tr>
</tbody>
</table>

The statistical fluctuations in the results indicate an error of 1% for the shielding length and 3% for the potential energy.

The Debye-Hückel theory predicts an infinite shielding length and a zero polyion potential energy for the definition of the shielding length and a zero polyion potential energy

C. Comparison with Debye-Hückel theory

The Debye-Hückel approximation to the small ion charge distribution about a central polyion at zero polyion concentration is given by

$$P(r) = \frac{K^2}{4\pi} \frac{e^{K(r-R_p)}}{1 + KR_p \cdot r}; r \geq R_p,$$

where $R_p$ is the polyion radius and $K$ is a constant which describes the degree of small ion shielding. In terms of the parameters used in this work

$$K^2 = \frac{8\pi Mq^2}{\epsilon kT L^3}$$

The net charge distribution can be obtained by integrating $P(r)$ over the volume exterior to the polyion and is found to be

$$W(r) = \frac{(1 + KR)}{(1 + KR_p) \cdot 1 + KR_p \cdot r}; r \geq R_p.$$  

Using equation (20) for the definition of the shielding length, the Debye-Hückel prediction is therefore

$$(1 + KR) e^{KR_p} = 0.1(1 + KR_p) e^{KR_p}.$$  

The polion electrostatic energy $U_p$ due to the small ion charge distribution can be calculated as follows:

$$U_p = \frac{1}{2} \int r^2 \rho(r) \phi(r) \phi(r),$$

where $\phi$ is the distance from the polyion center, $V$ is the volume of the polyion, $\rho(r)$ is the charge distribution inside the polyion (assumed to be spherically symmetric), $\phi(r)$ is the Debye-Hückel approximation to the potential, and $\phi_p(r)$ is the potential in the absence of the small ion charge distribution. The integral involving $\phi_p$ removes the polion self-energy as was similarly done in Eq. (16) for the calculation of the total electrostatic energy of the model system.

When the polyion charge distribution $\rho$ is spherically symmetric, the potential outside the polyion is a function of the net polion charge $Q$ but is independent of the functional form of $\rho$. In this region the Debye-Hückel approximation to the potential is

$$\phi(r) = \frac{Q}{\epsilon} e^{K(r-R_p)}; r \geq R_p,$$

and the potential in the absence of the small ion charge distribution is just the Coulomb potential

$$\phi_p(r) = \frac{Q}{\epsilon r}; r \geq R_p.$$  

Inside the polyion, $\phi$ and $\phi_p$ can differ by only a constant since they are both solutions to Poisson's equation $\nabla^2 \phi = \nabla^2 \phi_p = -4\pi j/\epsilon$. Since the potential is continuous at $r = R_p$, this difference is

$$\phi(r) - \phi_p(r) = \phi(R_p) - \phi_p(R_p) = \frac{Q}{\epsilon} \frac{K}{1 + KR_p}; r \leq R_p.$$  

The polion electrostatic energy is therefore

$$U_p = \frac{Q^2}{2\epsilon} \frac{K}{1 + KR_p}.$$  

When there are no byions present in the system, $M = 0$, the Debye-Hückel theory predicts an infinite shielding length and a zero polion potential energy $U_p$. This is because the polyion concentration is assumed to be infinitely dilute and the effects of neighboring polions are not taken into account. However, when the concentration of counterion-byion pairs is sufficiently high so that the shielding length is less than one-half the mean distance between polions, then the effects of a nonzero polion concentration should begin to become negligible. Under these circumstances, the predictions of the De-
Debye–Hückel theory should be comparable to the computer results.

Computer experiments were conducted on two systems. In the first, the zero charge polyion diffusion coefficient was $D_0 = 1 \times 10^{-6} \text{ cm}^2/\text{sec} (R_p = 21.43 \text{ Å})$ and in the second $D_0 = 2 \times 10^{-6} \text{ cm}^2/\text{sec} (R_p = 10.71 \text{ Å})$. The polyion concentration was 0.01 in both cases. As the number of neutral small ion pairs was increased, the calculated values of the shielding length and polyion potential energy approached those predicted by the Debye–Hückel theory. For sufficiently high $M$ values, the agreement was good. In Fig. 6 these results are shown for the case with $D_0 = 2 \times 10^{-6} \text{ cm}^2/\text{sec}$.

**SUMMARY AND CONCLUSIONS**

A computer technique for simulating the motion of ions in solution was presented and shown to obey classical statistical mechanics. The method was applied to a model polyelectrolyte solution with spherical ions. Several systems were treated and for each the small ion distribution function relative to a central polyion, the polyion electrostatic shielding length, and the average ion electrostatic energies were calculated.

The first systems treated contained no byions and only a sufficient number of counterions to balance the charge of the polyions. Neglecting small variations with polyion charge and concentration, the shielding length was given approximately by $r_s \approx 0.6L$, where $L^2$ is the volume per polyion. The total electrostatic energy was found to be proportional to the square of the polyion charge and the square root of the counterion charge.

The effects of adding counterion–byion pairs to the system was then studied. The shielding length decreased rapidly as more counterion–byion pairs were added. A comparison was made between the calculated values of the shielding length and polyion potential energy and the predictions of the Debye–Hückel theory for polyions at infinite dilution. As the shielding length became shorter than half the mean distance between polyions, the computer and Debye–Hückel results were in good agreement. Under these conditions the polyions appear to be effectively shielded from each other.

**ACKNOWLEDGMENTS**

The author wishes to thank Yin Yeh for a thorough reading of the paper and many helpful suggestions and discussion throughout the course of this work.

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16. The values of $R_p$ were calculated from a sequence of pseudo-random numbers generated within the computer. For a discussion on random and pseudorandom numbers see J. M. Chamberley and D. C. Handscomb, *Monte Carlo Methods* (Wiley, New York, 1964).


