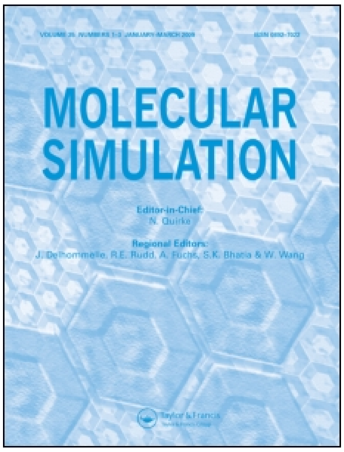

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Preliminary Communication

THE RADIAL BOUNDARY OF POLYELECTROLYTE SOLUTIONS CONTAINING ASYMMETRICAL SALTS

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Periodic boundary conditions are usually employed in the computer simulation of homogeneous systems. But the intrinsic homogeneity due to the infinite replication make them inappropriate for the treatment of inhomogeneous systems. In this case, the boundary of the system often consists in a hard wall which prevents the expansion of the system. The success of the so-called cell method is based on its simplicity. However several studies have reported undesirable surface effects when the cell method is employed in the simulation of water and ionic systems [1–5]. A number of alternatives to the cell method have been proposed [3, 6–9] but they are not commonly used. Probably this happens because the structural distortion is not grave and, especially, does not extend far from the cell wall. In this note we show that the cell method is not feasible when dealing with asymmetrical salts because the distortions at the boundary are severe. Besides we show that the extension to asymmetrical salts of one of the above mentioned alternative methods [9] is both simple and accurate.

In order to show the importance of the surface effects in the case of asymmetrical salts we have carried out a Monte Carlo simulation of a

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polyelectrolyte aqueous solution with 2:1 added salt. The polyion is modeled as a homogeneously charged soft cylinder with the same linear charge density as B-DNA and the effect of water is introduced through its dielectric constant. Two simulation boxes are used extending up to 37.3, and 45.5 Å respectively, from the polyion. The sample consists of 380 coions with charge −1 and 190 counterions of charge +2 plus 20 more counterions needed to cancel the portion of the polyion explicitly included in the simulation box (2 DNA turns). The larger system contains 580 coions and 290 + 20 counterions. Other details about the full interaction potential between the polyion and the mobile ions or the long range corrections along the axial direction are not relevant for the current discussion. The interested reader can find them elsewhere [9, 10].

Figure 1 displays the results for the charge neutralization function for a system at 1.2 M salt concentration. This function measures the fraction of polyion charge which is progressively canceled out by the solution ions. It can be seen in Figure 1 that the surrounding ionic cloud not only cancels the DNA charge but also overneutralizes it, a peculiar behaviour already observed in the case of monovalent added salt at high concentrations [10]. Apart of this structurally significant feature, it is to be stressed that the spurious surface effects induced by the boundary are much more important than in the monovalent added salt case [9]. The reason for this is that the neglect of the interactions beyond the cell boundary affects differently to anions and cations as they carry different charge. As a consequence, the coions tend to accumulate close to the wall while the opposite occurs for the counterions. The final result is a loss of the local charge neutrality which propagates inwards from the wall at distances where a bulk electrolyte would probably be found without the boundary. An increase of the cell radius does not improve significantly the results; the spurious maximum appearing close to the cell wall is even sharper in this case (Fig. 1).

We have recently proposed a method [9] to avoid the surface effects in polyelectrolyte solutions with a symmetrical added salt but the method needs slight modifications for asymmetrical salts. For completeness we first describe briefly the procedure for the former case. In our method, the simulation box is divided in two regions. The polyelectrolyte is placed in the center. There is an *inhomogeneous* region which covers approximately the zone of influence of the polyion (determined in the equilibration stage). The *homogeneous* region extends beyond this point. No physical barrier exists between both zones. Instead, in the homogeneous region the electrostatic interaction is progressively transformed into a short ranged potential using a modulating function. Hence the name given to the method,

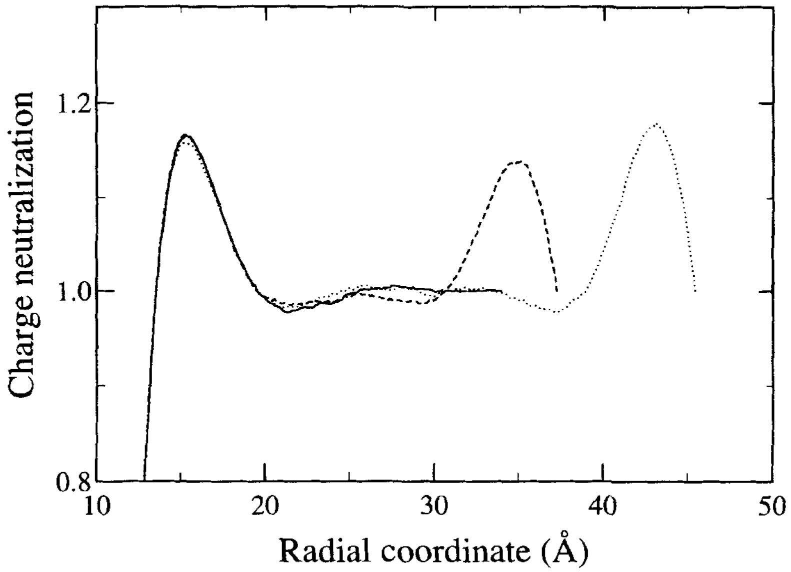

FIGURE 1 Charge neutralization functions for a polyelectrolyte system with 2:1 added salt at 1.2 M concentration. Full line, MBFB method; dashed, cell method with a 37.3 Å radius; dotted line, cell method with a 45.5 Å radius.

modulated bulk as a fuzzy boundary (MBFB). As the modulating potentials are short ranged, periodic boundary conditions are implemented at the end of the box in the radial direction. However, the modulation of the potential modifies the electrochemical potential and, then, it gives rise to a jump in the ionic concentrations. The jump is much less important than the abrupt change of the cell method (where it suddenly goes to zero) and, more importantly, it can be corrected by a variety of methods [11 – 13]. We have corrected it by measuring the difference of the mean energy at any point in the homogeneous region with respect to the correct bulk energy for ions interacting through the whole coulombic potential.

This procedure was designed to be used with symmetrical salts where the mean energy of anions and cations in the bulk region is the same. When the charges of the added salt are not symmetrical, coions and counterions at bulk have different mean energies and, thus, the correction potential should also be different. Figure 2 schematically displays the energy profiles and the meaning of the correction potentials. The polyion is placed at the left, outside of the figure. Region *P* denotes the inhomogeneous region and *T* represents the transition to the homogeneous zone *H*. In region *P* the counterion and coion energies are different from the bulk ones; the former increases with distance and the latter decreases. At some distance from

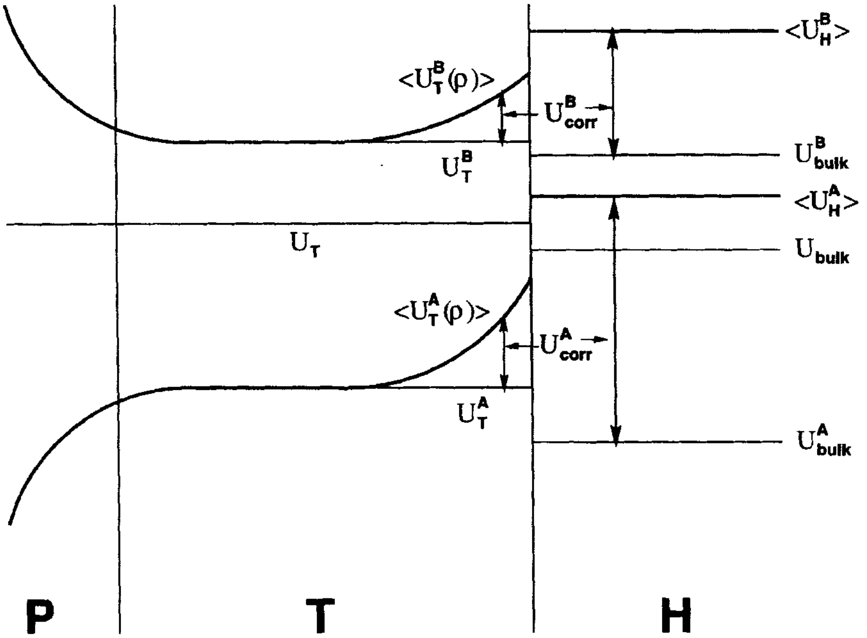

FIGURE 2 Schematic representation showing the energy profiles and the meaning of the potentials in the different regions (see the text).

DNA, the mobile ions do not feel its effect and their energy reach a plateau (at a different level due to the asymmetry in their charges). These are the bulk values of the energy, U_T^A and U_T^B. Contrarily to what happens in symmetrical salts, these values are distinctly affected by the discontinuity and differ somewhat from the actual bulk values U_{bulk}^A and U_{bulk}^B which are unknown at this stage. Before the end of the transition region, the potential energy of the ions begin to increase due to the progressive effect of the modulating potential, less favorable than the coulombic interaction. Finally, in the homogeneous region, where all the particles interact through the modulated potential, the mean potential energy of the ions is a constant for each of the species.

If the values of U_{bulk}^A and U_{bulk}^B were known, the effect of the modulating potential could be removed in the same way as for symmetrical salts, *i.e.*, by the addition of a correction term to the actual potential energy of every particle. The correction term (the shaded area in Fig. 2) for an ion $Z \equiv A, B$ in region H is

$$U_{\text{corr}}^Z = U_{\text{bulk}}^Z - \langle U_H^Z \rangle, \qquad (1)$$

and in T,

$$U^Z_{\text{corr}}(\rho) = U^Z_T - \langle U^Z_T(\rho)\rangle, \tag{2}$$

The methodological difference between symmetrical and asymmetrical salt is the knowledge of U^Z_{bulk} in the former case (see below). These bulk values may be obtained in a simulation of the corresponding electrolyte (*i.e.*, the system of interest with the polyion removed). But, in a standard Monte Carlo simulation, the final bulk concentration is not known in advance although it may be foreseen within a reduced range. More simple is its evaluation using an integral equation. It can be argued that we need a precise determination of the bulk quantities. Both methods are useful if, instead of the bulk quantities, the target calculation is the quotient

$$\gamma = U^A_{\text{bulk}}/U^B_{\text{bulk}}, \tag{3}$$

which remains essentially constant in small concentration intervals and which is very accurately obtained in integral equation treatments. Once γ is known, a first estimate of the bulk concentrations is given by

$$U^A_{\text{bulk}} \approx \frac{\gamma(n_A + n_B)}{\gamma n_B + n_A} U_T, \tag{4}$$

and

$$U^B_{\text{bulk}} \approx \frac{(n_A + n_B)}{\gamma n_B + n_A} U_T, \tag{5}$$

where n_A and n_B are the stoichiometric coefficients and U_T (see Fig. 2) is defined as

$$U_T = \frac{n_B U^A_T + n_A U^B_T}{n_A + n_B}. \tag{6}$$

Once the correction potentials are introduced in the simulation of the polyelectrolyte solution, the mean values of the potential energies obtained in the T and H regions begin to converge to the actual bulk value. The procedure is progressively refined in a consistent manner along the equilibration steps of the simulation. Notice that $\gamma = 1$ for a symmetrical salt. Thus, $U^A_{\text{bulk}} = U^B_{\text{bulk}}$ which enables its direct estimate through Eq. (4) from the mean values obtained for U^A_T and U^B_T in the former equilibration steps.

We have employed the MBFB as described above with γ calculated from the hypernetted chain integral equation. The simulation was identical to those using the cell method except the inherent methodological differences. We use an hexagonal prism of the same volume (and containing the same number of ions) as in the smaller hard cylindrical cell. The boundary between the T and H regions is at 29.5 Å. The results for the charge neutralization function are displayed also in Figure 1. After the maximum denoting overneutralization, there is a slight minimum but the DNA charge is canceled at about 30 Å and beyond that distance the system remains electroneutral at all distances. The more important point is that, contrarily to what happens for the cell method, the cancellation of the polyion charge does not show any distortion at the boundary limit when the MBFB method is used. Notice also that small but systematic departures between both simulations with the cell method and the MBFB results are observable at distances relatively close to the polyelectrolyte (about 20 – 25 Å) despite that the hard walls are as far from the axis as 37 and 45 Å respectively. This is especially important if one considers that the volume (or the number of particles) included in the region of valid results is only a small fraction – a 20 – 30 percent – of the total box volume in the cell method.

In this report we have focussed our interest in the disruption of the ionic symmetry caused by a disparity in the absolute value of the ionic charges. Notice that similar effects would be present when the symmetry is broken by a difference in the ionic sizes or in the strength of the repulsive interactions. Thus, simulations with the cell method should be looked with some prevention when any of the interaction potential parameters is such that it would lead to a system in which the bulk mean energies of anions and cations are different.

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