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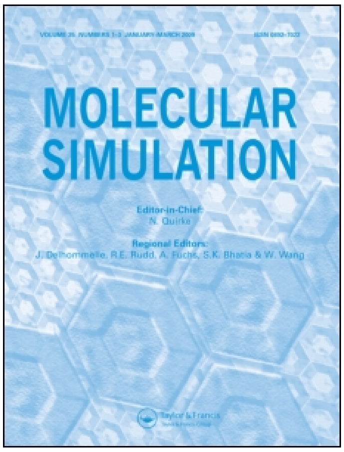

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A MODULATED BULK AS A FUZZY BOUNDARY FOR THE SIMULATION OF LONG-RANGED INHOMOGENEOUS SYSTEMS

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A new method for simulating infinitely diluted inhomogeneous systems with long-ranged electrostatic interactions is presented. The inhomogeneous system extends its effect through a cell of the appropriate symmetry which is in turn immersed in a box with bulk solution. The boundary between the inhomogeneous and homogeneous regions can be freely crossed by the moving particles. The particles interact with the surrounding bulk through a discrete particle-particle modulated (short-ranged) Coulomb potential while the missing tail is recovered as a mean field contribution computed in a self-consistent way. The bulk particles undergo usual periodic boundary conditions. The modulated bulk as a fuzzy boundary (MBFB) method is checked through Monte Carlo simulations of the cylindrical model of polyelectroyltes using soft continuous potentials. Comparison with cell model simulations of the same model is done.

KEY WORDS: Monte Carlo simulation, methodology, boundary conditions, inhomogeneous systems, polyelectrolytes

1. INTRODUCTION

Homogeneous systems are usually simulated employing the so-called periodic boundary conditions (PBC) to minimize edge effects due to the finiteness of the considered sample [1]. Suitable procedures to properly account for the long-range nature of coulombic and dipolar interactions in conjunction with PBC are well established. But the intrinsic homogeneity due to the infinite replication make the PBC inappropriate when inhomogeneous systems are treated unless one is just interested in an ordered phase of inhomogeneous constituents [2].

The simplest method to confine the system and prevent it from blowing up is the so-called cell model [3, 4] in which a (hard) container limits the volume available to the particles. Theoretical work on inhomogeneous systems often deals with the cell model due to its simplicity [5, 6]. Despite the general success of the cell model, simulation studies disclose undesirable surface effects as structural changes of water- like liquids [7, 8, 9] which propagate inwards from the walls several molecular diameters [10]. Furthermore, the dynamics of the moving species is affected by the presence of the boundary [11].

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Alternatives to the cell model for the simulation of inhomogeneous systems have been published [8, 12, 13, 14]. In these approaches, the sample is confined to a finite non-periodic volume using a constraint potential of some sort. The average contribution of the missing part of the system [12, 13, 14] (and its fluctuations which allows the dynamical properties of the simulated systems be similar to those of the real system [13]) must be included as well [13, 14]. Otherwise, if the inhomogeneous system (a polyelectrolyte for instance) is solvated with a layer of solvent of some thickness and the whole cluster simulated in vacuo, the surface tension tends to lower the surface area of the cluster, introducing a significant bias toward more spherical shapes, possibly distorting the simulated system [15].

The essence of the problem derives from the long range of the coulombic forces. Nevertheless, the inhomogeneity is not perceived at comparable distances. Hence the possibility of using effective short range potentials which are able to reproduce the structure of the bulk system. Potentials of this kind have proved to be useful in homogeneous ionic fluids [16]. Furthermore, it has been shown that the structure of these systems is almost identical when the electrostatic potential is modulated with appropriate termination functions [17, 18].

Our idea is to enclose the inhomogeneous area with a region of modified (short-ranged) ionic interactions. The transition area from the region with full coulombic interactions to that of the modulated potential acts as a '*fuzzy*' boundary separating the inhomogeneous part from the bulk solvent (or solution) so that the system is homogeneous on the outside. In the modulated bulk as a fuzzy boundary (MBFB) method, periodic boundary conditions can be used for the bulk and constraint forces are not necessary. Besides the supporting bulk is atomically detailed so there are no effects due to missing parts of the system. The global homogeneity does not conflict with the local anisotropy of the central system (i.e., because of the use of short-range electrostatic potentials in the external region the inhomogeneous part can not interact with its replicas).

2. THE MBFB METHOD

Consider a space-filling box, place inside the inhomogeneous entity (hereafter referred as polyelectrolyte) and fill it up with appropriate solvent (usually water molecules or electrolyte solution, hereafter referred as solvent). The resulting geometry represents an ordered phase of solvated polyelectrolytes. If one is interested in the infinitely diluted polyelectrolyte only the bulk particles must be allowed to interact with its replicas.

In the MBFB method the box is divided in two zones. The polyelectrolyte is centered in a cell of the appropriate symmetry inside the box. This region is the inhomogeneous or internal region I and may be regarded as the cell of the cell model although no real boundaries exist in the case. The rest of the box is the homogeneous, bulk or external region H. The size of the internal cell should be big enough so that a layer close to the boundary with the external region is not substantially influenced by the polyelectrolyte (*i.e.*, its charges are already almost completely screened). We call this layer the transition region, T, while the rest of the inhomogeneous zone (the part close to the polyelectrolyte) is denoted by P. The requisite of a transition region is not exclusive of our method. Indeed, the cell model requires a bulk-like phase near the walls [5, 19, 20], otherwise the state of the system is imprecisely defined. This may be overcome by performing the simulation in the grand-canonical ensemble where sampling at constant chemical potential (rather than concentration) unambiguously specifies the bulk phase [20].

The MBFB technique is suitable for many types of box geometries. In this paper the method is applied to a system for which the simulation box is the hexagonal prism sketched in Figure 1. There, two particles have been depicted. Particle H is a bulk particle which interacts with the rest of the system through a potential appropriate for the bulk (homogeneous) region. This potential must be short-ranged, its range r_c being lower than the thickness of the transition region R^T so that the bulk particles do not interact with the polyelectrolyte region, *i.e.*, the bulk particles feel only homogeneous media (homogeneous and transition regions). Consequently, bulk particles undergo periodic boundary conditions to properly account for the replicas of the homogeneous region. To fulfill third Newton's law, the particles in the transition zone interact with those in the external region through the same potential. Thus, particle I perceives both the polyelectrolyte and a external bulk, giving the desired continuity to the system. (Obviously, particles in the inhomogeneous region interact with each other through full long-ranged potentials as in the cell model). This is clearly an improvement over the plain cell model in which interactions with the part outside the cell are neglected. To avoid indirect with the inhomogeneous entity, the minimum thickness of the bulk region (R^H in figure 1) should exced the bulk potential range r_c. In this way a particle in

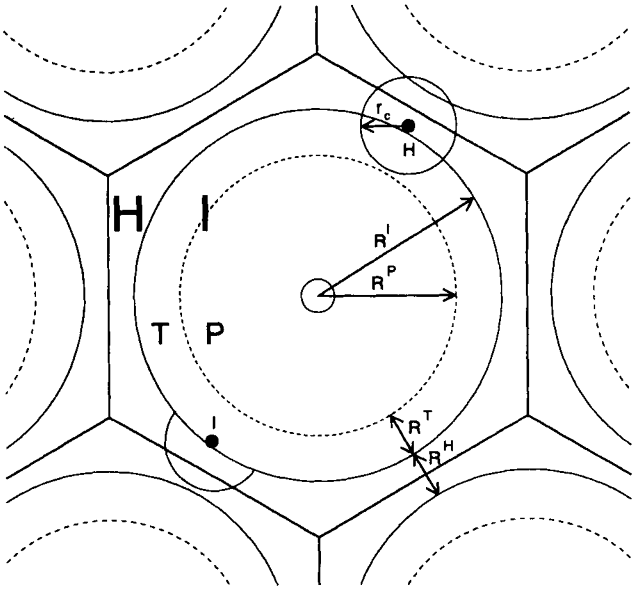

Figure 1 Geometry of the model. The labels in each region have the following meaning: H, homogeneous; I, inhomogeneous; T, transition; P, polyelectrolyte. The small circles with radius r_c around the two particles drawn comprise the zone in which those particles interact through the modulated coulomb potential (see the text).

the transition region does not interact with the transition region of image boxes (see particle *I* in Figure 1).

The lack of impenetrable boundaries in the MBFB method allows the free movement of particles between regions producing fluctuations of density and charge. As a particle in the inhomogeneous zone interacts with all other particles in that region with full coulombic potentials, it is essential to ensure that the region is electroneutral in average. As shown in following sections, this is fulfiled if suitable sizes of the system are used.

3. THE CASE OF THE CYLINDRICAL POLYELECTROLYTE

In this section we describe the applicability of the MBFB method to the simulation of the cylindrical model of polyelectolytes [4]. In this model, the polyelectrolyte is regarded as a infinitely long rigid cylinder bearing a uniform axial charge density characterized by the parameter b, the length of a polyion segment incorporating one electronic charge. The solvent is treated at the McMillan-Mayer level, *i.e.*, it is considered as a dielectric continuum. For the inhomogeneous region, a cylinder coaxial with the polyelectrolyte is used in correspondence with the cell model. The infinite length of the polyion is mimicked applying periodic boundary conditions in the axial direction. (In the MBFB simulations the fuzzy boundary is used only in those directions exhibiting anisotropy; those perpendicular to the cell axis in this work). The net charge of the polyelectrolyte is compensated by an appropriate number of monovalent counterions and added salt at a given concentration is present. As for the shape of the simulation box we have choosed an hexagonal prism because the hexagon is the plane-filling polygon that includes a circle with minimum excess area. (If the MBFB method is to be applied to a radial symmetric case, a sphere should be used for the central cell while the truncated octahedron or rhombic dodecahedron for the simulating box would minimize the volume of 'uninteresting' bulk region [21, 22]).

A number of alternatives exist for short-range potentials satisfactorily describing the bulk region. We have chosen a modulated coulombic interaction described by Brooks *et al.* [17]: the coulombic potential $U_{ij}^{\mathrm{cou}}(r_{ij})$ is modified through the relation

$$U_{ij}^{\mathrm{mod}}(r_{ij}) = U_{ij}^{\mathrm{cou}}(r_{ij})S(x) \tag{1}$$

in which $x = r_{ij}/r_c$, r_{ij} the distance between ions i and j, r_c the range of the potential as said above, and the modulating function $S(x)$ is

$$S(x) = \begin{cases} 1 - 2x^n + x^{2n}, & x < 1 \\ 0, & x \geqslant 1. \end{cases} \tag{2}$$

The particular functionality of the terminating function produces a smooth decay to zero so that both the potential and its derivative are continuous everywhere.

It has been proved that the structure of the TIPS water and a electrolyte solution model are properly described by this potential (using $n = 1$ and $n = 2$ respectively, MEI4 and MEI5 in Brooks' terminology [17]). Even dynamical properties such as the velocity autocorrelation of SPC water are correctly modeled when the coulombic potential is modulated [18] (best with $n = 1$). We have carried out several simulations of bulk electrolyte solutions with mono and divalent ions using both the full and modulated Coulomb potential with $n = 1$ observing that the structure (as given by the radial distribution function $g(r)$) is essentially the same in all comparable pairs of simulations. Even more sophisticated tests as cluster structure [23], percolation properties [24] and Voronoi polyhedra analysis [25] display no significant differences. Therefore, both water models and electrolyte solutions are not substantially distorted when the long-range coulombic potential is replaced by the short-range modulated Coulomb potential, so it fits all the requirements to act as the 'bulk' potential of the MBFB method. The success of this modulated potential lies in the fact that the effect of the missing long coulombic tail is properly balanced by the modification of the interaction given by the modulation at short and medium distances. Other termination schemes that shorten the range of the Coulomb potential to a finite extent by modifying the interaction only for distances slightly lower than the cut-off affect significantly to the system structure [17]. In this sense the switching function traditionally used in some commercial simulation packages has been explicitly not recommended for the simulation of ions and their interactions with biomolecules [26].

Although the structures obtained with the modulated Coulomb potential are correct, the actual values of thermodynamic properties are not, as is the case of any short range effective potential [16]. For example, the chemical potentials of a bulk electrolyte obtained using the modulated and the full coulombic interactions are different. As the internal and bulk regions are adjacent, the system evolves to make equal the chemical potential at both sides of the boundary which is accomplished by a jump of density at the boundary. Notice the similarity with the self-consistent Monte Carlo method of Vorontsov-Velyaminov and Lyubartsev [27] in which two regions (one with discrete particles and other described through density profiles) are in contact. The density discontinuity is given by the difference between the chemical potentials

$$\rho_i^{\text{cou}}/\rho_i^{\text{mod}} = \exp\left[\beta(\mu_i^{\text{mod}} - \mu_i^{\text{cou}})\right]. \tag{3}$$

In Figure 2 the long dashed lines (representing the density profiles of the co- and counter-ions of a state described below) show a sudden drop when passing from the inhomogeneous to the homogeneous region. To avoid this effect, the appropriate bulk properties must be corrected. In related situations this has been done in different ways. Clarke *et al.* [16] use a first order perturbation theory. Linse [28] employs a reference hypernetted chain (RHNC) scheme. Vorontsov-Velyaminov *et al.* [27] measure the density at both sides of the discontinuity and use equation 3 to self-consistently correct the chemical potential. In this study, a correction energy is added to the actual values of the energy calculated at every step of the simulation so that the average energy of the ions at both sides of the boundary is equal to the bulk energy, U^{bulk} (that of the ions interacting via the coulomb potential far away from the polyelectrolyte). The correction is then the difference between the average energy of the ions at a distance r_{ip} from the polyelectrolyte and U^{bulk}

$$\begin{aligned} U^{\text{corr},T}(r_{ip}) &= U^{\text{bulk}} - \langle U(r_{ip}) \rangle \\ U^{\text{corr},H} &= U^{\text{bulk}} - \langle U^{H} \rangle. \end{aligned} \tag{4}$$

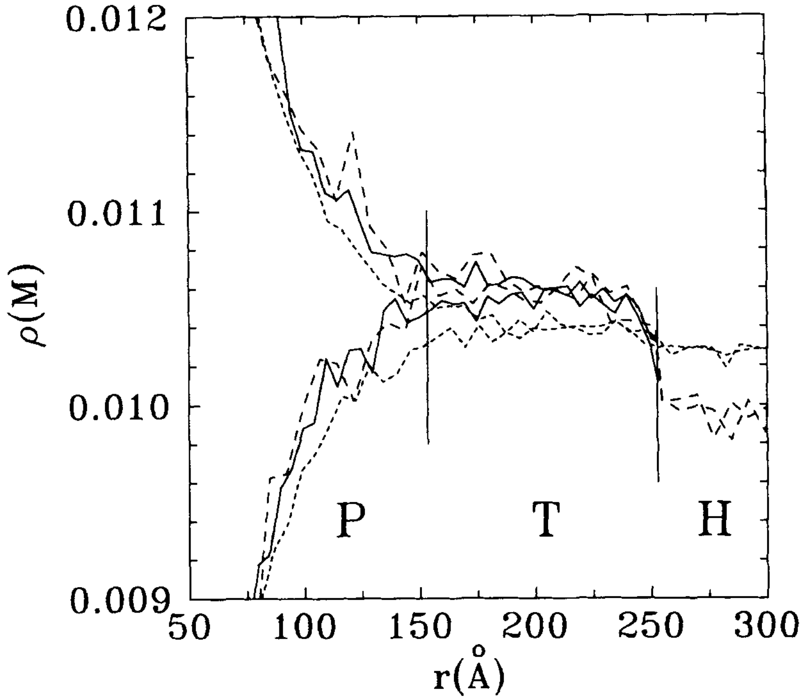

Figure 2 Details of the radial concentration profiles far from the polyelectrolyte for a cell model (C^D, solid lines) and a MBFB (M^E, short dashed lines) simulations of the 0.01 M system. The MBFB profiles computed prior to introducing the correction potential are also shown (long dashed lines).

The angles denote averages within the region indicated by the superscript. U^{bulk} has been evaluated along the equilibration stage of the simulation. As every ion in the H region interact with each other through the modulated potential all of them have (in average) the same energy $\langle U^H \rangle$ and, thus, $U^{\mathrm{corr},H}$ is a constant. On the other hand, an ion placed just in the inner side of the boundary interacts through the modulated potential only with those in the homogeneous region (see ion I in Figure 1). Then its correction potential is smaller than $U^{\mathrm{corr},H}$, and smaller the farther from the boundary decaying to zero at distances (from the boundary) higher than the modulation radius r_c. Thus, the bulk energy must be evaluated (as the average of the energies of co- and counterion) as far as possible of both the boundary and the polyelectrolyte, *i.e.*, at the plateau of the energy curves (see Figure 3).

In summary, the full set of potentials in each region of the simulation box (polyelectrolyte, transition and homogeneous) is:

$$\begin{aligned} U^P(r_{ip}) &= \Sigma^{P,T}\, U^{\mathrm{ions(cou)}} + U^{\mathrm{poly}} \\ U^T(r_{ip}) &= U^P + \Sigma^H\, U^{\mathrm{ions(mod)}} + U^{\mathrm{corr},T} \\ U^H &= \Sigma^{T,H}\, U^{\mathrm{ions(mod)}} + U^{\mathrm{corr},H} \end{aligned} \tag{5}$$

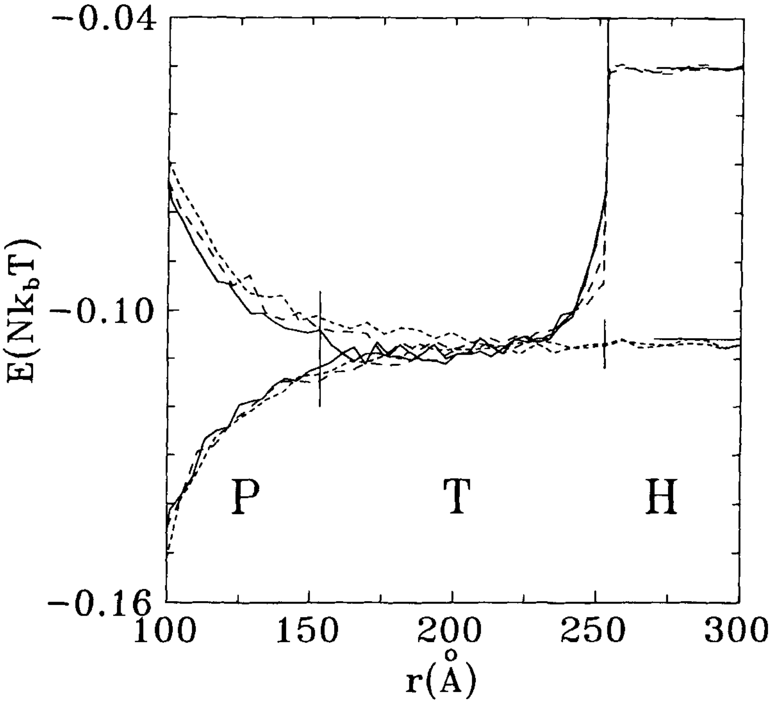

Figure 3 Details of the average energy of ions far from the polyelectrolyte for the 0.01 M system. The simulations and line types as for the previous figure.

where the upper lables *P*, *T* and *H* indicate the region(s) in which the sum takes place, 'poly' refers to the interaction with the polyelectrolyte and 'ions' to the interaction with another ions which include either the full coulombic potential or the modulated one.

4. MODEL POTENTIALS AND SIMULATION DETAILS

The interaction between ions has two terms: the electrostatic (full or modulated) and the repulsive one. The repulsive potential is of the form [5, 23, 29]

$$U_{ij}^{rep,ions}(r_{ij}) = \frac{A_M e^2 |z_i z_j|}{N_c n(r_i + r_j)} \left(\frac{r_i + r_j}{r_{ij}} \right)^n. \tag{6}$$

Here $A_M = 1.7476$ is the Madelung's constant of the NaCl structure, $N_c = 6$ the coordination number of the same structure, $n = 9$ the steepness parameter of the repulsive interaction, z_i the electrovalence of ionic species i ($\pm$ 1 in this study) and r_i its nominal radius. The value $r_i = 1.4214$ Å, taken for both anions and cations, gives a bulk electrolyte structure corresponding to a RPM hard-sphere diameter of 4.2 Å [29]. This size has been used in other studies [20, 23, 27] and roughly corresponds to a monovalent ion with the account of its hydration shell [27, 30].

For the repulsive interaction of the small ions with the polyelectrolyte an equivalent functionality is used [5]

$$U_{ip}^{\mathrm{rep,poly}}(r_{ip}) = \frac{K_p e|z_i|\xi}{r_i + r_p}\left(\frac{r_i + r_p}{r_{ip}}\right)^n. \tag{7}$$

The parameters $r_p = 9$ Å and $K_p = 1.4510.10^{-12}$ Jm/C are chosen to produce the maximum in the counterion radial density profile at about $r_{ip} = 11$ Å, representative of DNA (a value between 12Å—the distance from the center of an hydrated Na ion to the B-DNA helix axis in the phosphates region [31]—and 10 Å used in other soft rod simulations [5, 32]).

The coulombic interaction between an ion and the finite segment of the charged rod within the simulation box (of height L) is [19]

$$U_{\mathrm{ip}}^{\mathrm{box,poly}}(r_{ip}) = -2z_i\xi\beta^{-1}\sinh^{-1}\left(\frac{L}{2r_{ip}}\right). \tag{8}$$

It is well established that, in computer simulation of anisotropic systems, the interactions of each particle with the part of the system along the direction where periodic boundary conditions are used must be included [33]. This is due to the fact that the anisotropic charge distribution is repeated *ad-inifitum* in those directions. Although the Ewald method traditionally used in homogeneous ionic simulations has been developed for systems replicated along two [34] and one [27] directions, we prefer the method adopted by most researchers in this area [5, 19, 20, 32]. In this method, pioneered by Torrie and Valleau for the case of the planar electrical double layer [33], the effect of the whole charge distribution outside the simulation cell is included as a mean field term computed self-consistently from the average charge distribution within the cell. The contribution from the replicas in the axial direction has the form

$$U_i^{\mathrm{inf}}(r_{ip}) = U_i^{\mathrm{inf,ions}}(r_{ip}) + U_i^{\mathrm{inf,poly}}(r_{ip})$$

$$U_i^{\mathrm{inf,ions}}(r_{ip}) = 2z_i\lambda_B\beta^{-1}\int_0^{R'} B(r_{ip}, r')Q(r')r'\,dr' + U^*$$

$$B(r_{ip}, r') = -\int_0^{2\pi} \ln\left(\frac{L}{2} + \sqrt{\left(\frac{L}{2}\right)^2 + r_{ip}^2 + r'^2 - 2r_{ip}r'\cos\phi}\right)d\phi$$

$$U_i^{\mathrm{inf,poly}}(r_{ip}) = 2z_i\xi\beta^{-1}\log(r_{ip}) - U_{ip}^{\mathrm{box,poly}}(r_{ip}) - U^*. \tag{9}$$

R^I is the radius of the cell and $Q(r_{ip})$, the total radial charge density at a distance r_{ip} from the polyion, is given by

$$Q(r_{ip}) = \sum_i z_i\rho_i(r_{ip}) \tag{10}$$

(the sum extends over all charged species and $\rho_i(r_{ip})$ is the radial density of species i). Besides, in equation 9, $\xi = \lambda_B/b$ is the reduced axial charge density of the polyion, λ_B

being the Bjerrum length

$$\lambda_B = \frac{e^2\beta}{4\pi\varepsilon\varepsilon_0} \tag{11}$$

where e is the magnitude of the electronic charge, $\beta = 1/(k_\beta T)$, k_β is the Boltzmann constant, T is the temperature, ε_0 is the vacuum permitivity and ε is the (relative) dielectric constant of the pure solvent. In equation 9 the term U^* (which ultimately cancels between the polyelectrolyte $U_i^{\mathrm{inf,poly}}$ and ions $U_i^{\mathrm{inf,ions}}$ contributions) depends on the axial length considered to compute the external potential and diverges when the full infinitely long system above and below the central box is accounted for [19]. For this reason, in numerical work, the interaction with the infinite charge distribution is not split in polyion and small ions contributions.

Special care must be taken in the calculation of U^{inf} on the MBFB simulations. The cell model *imposes* the global electroneutrality of the simulation cell even though the system may not be extensive enough to allow the relaxation of the concentration profiles. As the MBFB method allows fluctuations of charge in the I region, the net charge of the mobile ions within that zone may not exactly cancel the polyelctrolyte charge (see the discussion on the charge compensation function below). However, for the computation of U^{inf} an electroneutral system is required; otherwise we infinitely add up the contribution of a net charge. Fortunately the correction is not sensitive to the details of the charge distribution at long distances so we decided to add to the last histogram bin (of $Q(r_{ip})$) the remaining charge thus ensuring electroneutrality. Proceeding this way, the U^{inf} potentials from cell model and MBFB simulations have been found to agree satisfactorily.

At the beginning of the simulations, the correction potentials of equations 4 and 9 are both unknown, so they are taken as zero; they must be self-consistently computed during the simulation. The simulations start by randomly placing the small ions in the box but avoiding overlaps between particles. The system is then pre-equilibrated for a relatively small number of cycles. Then, the potential energy profiles are computed so that a first set of correction potentials (equation 4) can be obtained. With the corrected potentials, the system is allowed to relax for a while; in this period the jump of density at the border of the homogeneous and inhomogeneous regions vanishes (see fig. 4). Now, the density profiles are computed and the U^{inf} contribution to the potential (equation 9) estimated. The system finishes its equilibration with a further period so that the correction potentials and U^{inf} attain self-consistency.

5. SIMULATION RESULTS

Monte Carlo simulations have been performed with the cell model and the MBFB methods for a model of native DNA ($\xi = 4.2$ [35]) in supporting electrolyte solution. The dielectric constant of water $\varepsilon = 78.358$ and the temperature 298 K lead to a value of $\lambda_B = 7.1524$ Å. The parameters allow the comparison with previous simulations of the cell model. The concentrations of supporting monovalent electrolyte are $C = 0.001, 0.01$ and 0.9 M (values of the average coion concentration). These concentra-

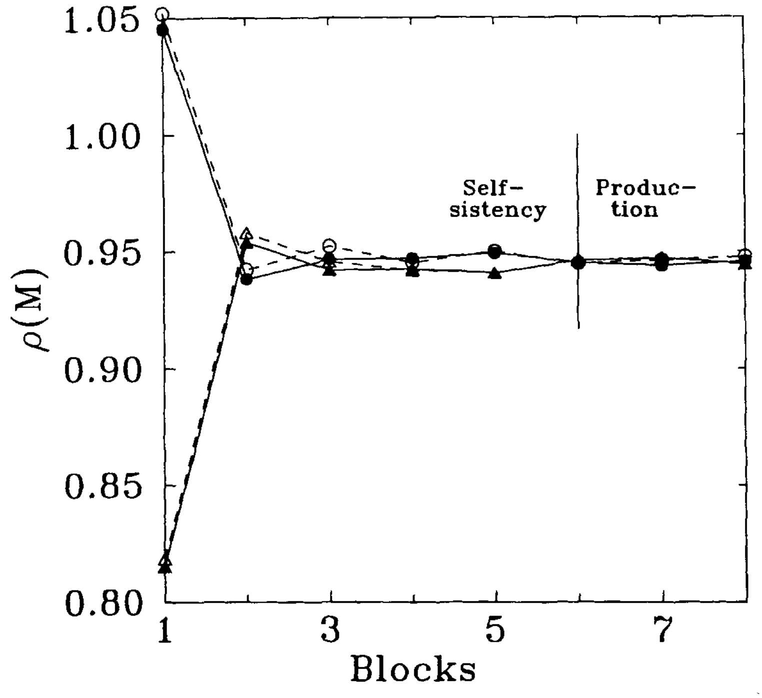

Figure 4 Coion (filled symbols) and counterion (open symbol) concentration at the internal (circles) and external (triangles) side of the boundary between the homogeneous and inhomogeneous region along the M^B simulation. Each block is 1.2 million single particle moves long.

tions cover a broad range to check the ability of both methods to simulate the cylindrical polyelectrolye. The two lowest concentrations have been previously addressed by Murthy *et al.* [5] whose results serve us as a further check. The higher concentration is motivated by the particular properties exhibited by highly charged electrolyte solutions [38, 23]. In fact, the interesting salt-induced transition from the B and Z forms of the DNA appears to about 2.3 M NaCl concentration [36].

The number of neutralizing counterions N_+ and the axial length of the simulation box are related through $L = N_+ b$. The number of ionic pairs of excess salt N_{+-} and its concentration give the total volume available to the particles. The total simulation box volume is obtained adding a somewhat arbitrary polyelectrolyte excluded volume. We have used a radius of 7 Å for the polyelectrolyte core, value which is supported by the resulting density profiles. The modulating radius r_c have been chosen so that the interaction sphere of a bulk ion include about other 50 ions in the average, which corresponds to $r_c = 204, 100$ and 22 Å for $C = 0.001, 0.01$ and 0.9 M respectively. Including 50 ions is probably too conservative. The bulk electrolyte could correctly be described by the modulated coulomb potential even if much less ions would be seen by the average ion [17]. The numerical details of the simulations are summarized in Table 1. The number of steps includes both those corresponding to the self-consistency of the correction potentials and the production periods. In every case, at least one thousand attempted moves per particle were used in the pre-equilibration stage. Most MBFB

Table 1 Simulation details

Run label	*C(M)*	*Simulation model*	*No. of ions* $N^{(a)}_{+-}$	$N^{(b)}_{+}$	*Geometry*[c] *(Å)* *L*	R^I	*Ap*	*Single particles moves* × $10^{-6(d)}$
C^A	0.9	Cell	210	30	51.1	49.6		3.5 + 12.5
C^B		Cell	300	30	51.1	59.4		4.2 + 4.8
M^A_1		MBFB	210	30	51.1	36.0	47.3	5.5 + 3.0
M^B		MBFB	300	30	51.1	45.0	56.3	6.6 + 3.6
M^A_2		MBFB	210	30	51.1	45.0	47.3	5.5 + 3.0
C^D	0.01	Cell	124	60	102.2	253.4		4.0 + 8.0
C^E		Cell	200	60	102.2	321.7		5.5 + 4.0
C^F		Cell	390	117	199.2	321.7		6.2 + 12.8
M^E		MBFB	200	60	102.2	252.7	306.4	9.5 + 10.0
M^G		MBFB	200	0	102.2	252.7	306.4	4.5 + 5.0
M^F		MBFB	390	117	199.2	252.7	306.4	9.9 + 5.4
C^H	0.001	Cell	700	240	951.5	408.7		12.0 + 9.0
M^H		MBFB	350	120	802.6	204.4		9.2 + 4.8
M^I		MBFB	700	240	802.6	408.7		16.5 + 9.0

[a] Number of ionic pairs of excess salt.
[b] Number of neutralizing counterions.
[c] Box height, cylindrical cell radius and hexagon apotheme respectively.
[d] Self-consistency and production periods (see the text).

simulations have an equivalent cell model simulation with the same number of particles to allow comparison. The simulation labelled M^G was performed with an uncharged polyelectrolyte and is used as a reference.

In Figure 3 the average energies of coions and counterions in the system at 0·01 M concentration using different simulation methods are shown in detail. The cell model simulation C^D has a cell radius R^I similar to that of the MBFB simulation M^E. The energies for anions and cations are different due to the effect of the polyelectrolyte up to about 170 Å where both converge to the bulk value. The cell model energy curve has a turn-up beginning at about $r = 230$ Å, due to the absence of ions outside the cell. The average energy at the cell wall is about $-0.076\, k_\beta T$ units per particle, and has a infinite value outside the cell. The uncorrected MBFB energies also exhibit the turn-up although it is less pronounced as the particles in this area do interact with the external region (although though a modified potential), and have a non-infinite value in the homogenous region (about -0.050, which agrees with the mean energy we have obtained in a MC simulation of the homogeneous electrolyte—*i.e.*, in absence of polyelectrolyte—at roughly the same bulk concentration using the modulated coulomb potential which is -0.049 ± 0.001). In this sense, the MBFB method is better than the cell model even when the correction of equation 4 is not included. When the correction is taken into account, the coion and counterion energies converge to a bulk value ≈ -0.108 and remain there across the boundary between regions and through the homogeneous region. The small straight lines at the rightmost side of the figure represent the energy for the uncharged polyelectrolyte simulation M^G with and without the correction energy. They should be coincident with the corresponding bulk energies of the charged polyelectrolyte simulation (in equivalent conditions). This is satisfactorily fulfilled (see Table 2 for numerical values). Although the coion and counterion

Table 2 Selected numerical results.

	C^{bulk} $(mM)^{(a)}$		*Average energy* $(-Nk_BT)$			
Run label	*Internal*	*External*	*Internal*	*External*	*Internal region net charge* (*e*)	R_M $(\text{Å})^{(b)}$
$C^{A(c)}$	$967^{(d)}$		$0.515^{(d)}$			$14.00^{(d)}$
	968		0.519			
C^B	950		0.514			14.01
	950		0.518			
M_1^A	966	965	0.515	0.513	0.02 ± 0.06	14.07
	967	963	0.513	0.513		
M^B	946	943	0.515	0.515	0.03 ± 0.08	14.09
	948	944	0.519	0.516		
M_2^A	968	960	0.517	0.517	-0.01 ± 0.09	14.08
	969	959	0.519	0.516		
C^D	10.56		$0.108^{(e)}$			31.4
	10.58		0.107			
C^E	10.34		—			29.9
	10.38		—			
	$10.32^{(f)}$					31.0
C^F	10.36		0.108			31.3
	10.38		0.109			
M^E	10.38	10.28	0.107	0.107	0.06 ± 0.13	31.3
	10.40	10.28	0.108	0.107		
M^G	$10.00^{(g)}$	9.98	0.105	0.106	0.04 ± 0.15	
M^F	10.34	10.34	0.110	0.109	0.06 ± 0.09	31.0
	10.36	10.34	0.107	0.109		
C^H	1.032		0.0362			52.6
	1.033		0.0372			
M^H	1.032	1.028	0.0340	0.0346	—	52.4
	1.032	1.026	0.0365	0.0349		
M^I	1.029	1.032	0.0366	0.0364	0.10 ± 0.12	52.4
	1.032	1.031	0.0360	0.0364		

[a] Bulk concentration.
[b] Manning radius.
[c] First and second rows are values for coions and counterions respectively.
[d] Estimated uncertainties affect the last figure.
[e] The energy from a MC homogeneous simulation of the 0.0105 M electrolyte is -0.109 ± 0.001.
[f] Coions and counterions average from reference [5].
[g] Anions and cations average.

energies are not exactly equal at the radial distance at which the transition region begins the correction energy is not appreciable until the second half of this region. This, together with the fact that the curves are approximately symmetric, allows to calculate the correction energies U^{corr} from the beginning up to half the T region.

The concentration profiles for the same systems (C^D and M^E) are given in Figure 2. Only an enlargement of the region of interest to this paper is depicted as the overall curves closely match those given by Murthy *et al.* for the cell model [5]. The uncorrected MBFB curves are similar to those of the cell model up to the transition between regions. The cell model profiles end at the wall while the uncorrected MBFB ones manifest the jump in density, as commented above. The bulk value of the corrected profiles is between those uncorrected in T and H regions. Besides, this bulk concentration agrees with that for the cell model simulation C^E which uses the same number of particles as M^E.

As commented above, the density profiles of our 0.001 and 0.01 M simulations agree with previously reported investigations. For this reason, for these systems we only give some selected numerical results (Table 2). Nevertheless, as far as we are aware, the system at 0.9 M concentration of supporting electrolyte has not yet been previously studied. The radial concentration profiles of coions and counterions for a cell model and a MBFB simulations of this system (C^B and M^B respectively) are displayed in Figure 5. The agreement between both simulations is as satisfactory as in the case of the diluted systems. The bulk concentrations in the cell model simulations were estimated from the average of the density profiles in the bulk-like region near the cell boundary. The region closest to the wall should be excluded from this average because the neglect of the interactions with the medium beyond the cell distorts the homogeneity of this area, usually producing drying of the wall. Although this effect for atomic fluids is small (Valleau claims that "the boundary layer of the restricted primitive model at an uncharged hard surface is electrically homogeneous" [37]) and apparently has been neglected in most cell model simulations, we have clearly detected it in our density profiles, especially in the $C = 0.9$ M simulations, as can be seen in Figure 5. This is overcome in the MBFB simulations in which the existence of the bulk region

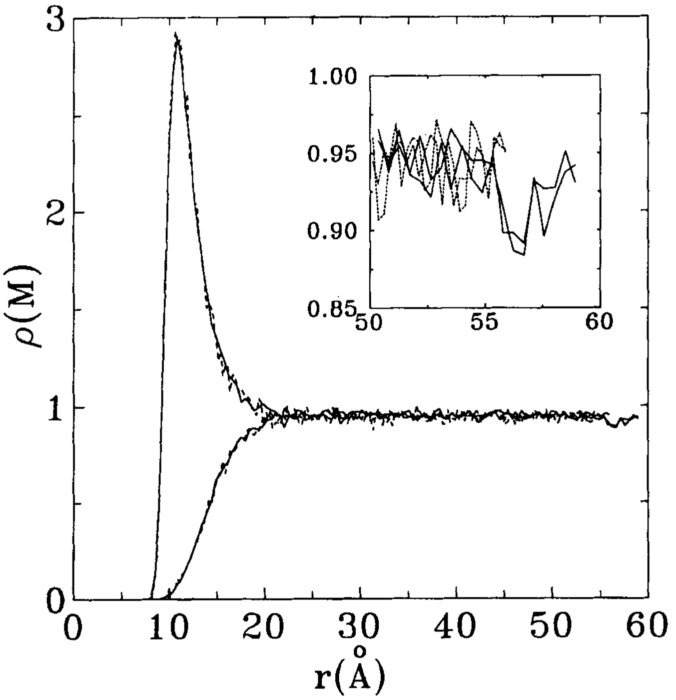

Figure 5 Radial concentration profiles of coions and counterions for a cell model (C^B, solid lines) and a MBFB (M^B, dashed line) simulations of the 0.9 M system. The inset is an enlargement of the region near the wall of the cell model simulation showing the distortion that causes in the ions concentration.

ensures a correct homogeneous density. In table 2 the estimates of the bulk concentration at both sides of the boundary (internal and external) are given for the MBFB simulations.

The bulk concentration decreases with increasing size of the simulation box in the direction perpendicular to the polyelectrolyte, *i.e.*, as the average counterion or polyion monomer concentrations decrease. This effect is related with the fundamental measure of non-ideality in a polyelectrolyte solution, the so-called preferential interaction coefficient, which has been extensively studied by grand canonical MC techniques [39]. Globally, the bulk cell model and the internal MBFB values coincide for simulations with the same ratio of neutralizing to added counterions (N_+/N_{+-}), for example the runs C^E, C^F, M^E and M^F. This reveals that the MBFB simulation method does not require more particles than a cell model one to describe a particular polyelectrolyte/bulk state.

In the M^E simulation, the modulating radius $r_c = 100$ Å is larger than half the axial length of the box $L/2 = 51.1$ Å. As the minimum image is always used in the axial direction, the modulated interactions for this system are not correctly treated. This is a consequence of the large modulating radii used. This effect leads to a slight departure between the internal and external bulk concentrations, 10.39 and 10.28 mM respectively. When the height of the box is (almost) doubled, M^F run, so that $L/2 \approx r_c$, this small distortion fully disappear. The same ocurrs in the pair of simulations M^H and M^I for $C = 0.001$.

The way in which the mobile ions gradually cancels the polyion charge is described by the excess charge $q(r_{ip})$ given by

$$q(r_{ip}) = \int_0^b \int_0^{2\pi} \int_0^{r_{ip}} Q(r')r'dr'\,d\phi\,dz. \tag{12}$$

This function is zero at $r_{ip} = 0$ and increases with distance reaching the unity at the bulk region. The behavior of $q(r_{ip})$ is particularly useful in assessing the effects of the boundaries in simulations [5]. In Figure 6 the excess charge functions for simulations at $C = 0.01$ M are shown. The cell model and MBFB M^F curves are indistinguishable within the statistical noise. The scale has been extremely enlarged to make appreciable the small departures of the MBFB M^F curve. This small effect is due to the fact that the modulating radius is larger than half the simulation box height as said above. Leaving this aside, at any concentration, MBFB simulations give charge cancellations almost indistinguishable to those of the cell model with the same number of ions. This is the strongest test that ensures that the MBFB method works properly. Related with the excess charge is the so-called Manning radius R_M, defined as the radius of the area around the polyelectrolyte in which a fraction $1 - \xi^{-1}$ of its charge is cancelled by the small ions charge (our $\xi = 4.2$ implies that $q(R_M) = 0.7619$). It corresponds to the area of the condensed ions in Manning's counterion condensation (CC) theory [35]. Our results agree with Murthy's who gives $R_M = 31.0$ Å for a simulation with the same parameters as our C_2^B and $R_M = 52.2$ Å for a simulation with $C = 0.001$ M. Finally, as can be seen in Table 2, all our MBFB simulations fulfill the requirement that the net charge of the internal region must be zero.

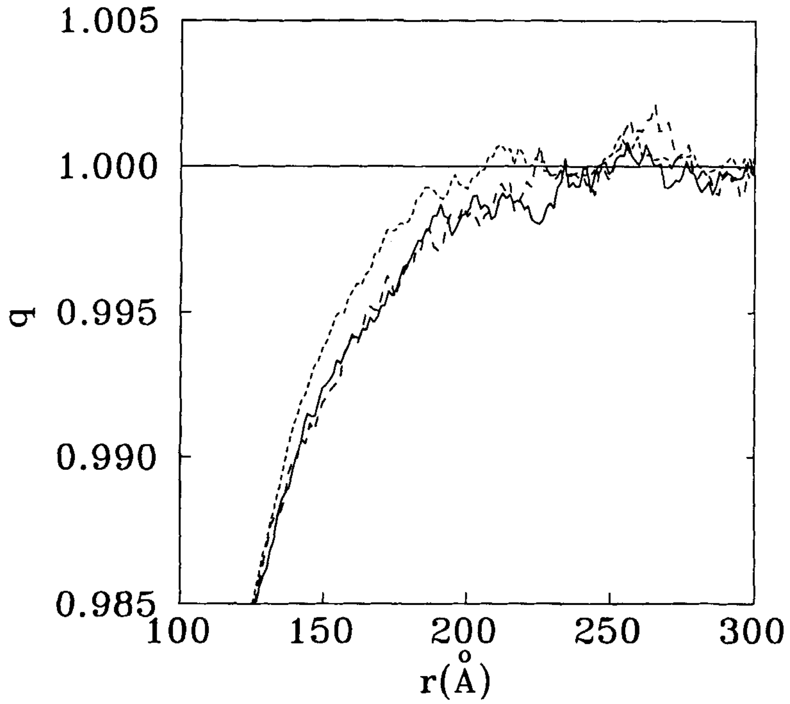

Figure 6 Excess charge $q(r_{ip})$ for a cell model (C^F, solid line) and two MBFB (M^E, short dashed line; M^F, long dashed line) simulations. Notice the enlargement of the $q(r_{ip})$ scale.

6. CONCLUDING REMARKS

We have shown that the modulated bulk as a fuzzy boundary method is able to simulate infinitely diluted long-ranged inhomogeneous systems without using impenetrable boundaries. The results for which the hard wall of the cell model has no significant influence are correctly reproduced by the MBFB method. It is worth noting that the bulk region of the MBFB method is not a mere adding to the cell model but plays a fundamental role in defining the correct structure of the system. Thus, no more particles are needed in a MBFB simulation than in the cell model for the same thermodynamical state. In fact, the absence of forbidden regions slightly improves the statistical efficiency of the MBFB methods in Monte Carlo simulations with respect to the cell model in which typically a ten percent of the moves are rejected due to collision with the wall [5, 32]. The method is expected to be particularly useful in the simulation of systems with molecular solvent and in dynamical studies. Investigations in this line are being performed in our laboratory.

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Note added in proof: Eurther investigations at higher concentrations and/or for divalent ions show that the spurious effects of the cell-model wall dramatically increase. The method described in this article works well also in these conditions.

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