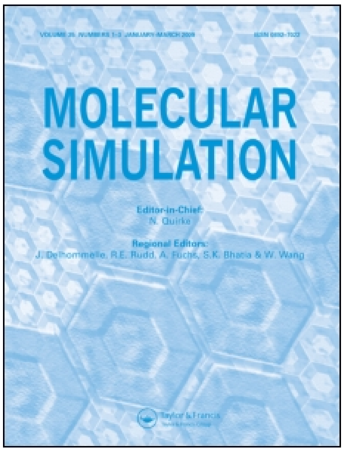
This article was downloaded by:
On: *14 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

The Glassy Wall Boundary for Simulations of Inhomogeneous Systems

Heather L. Gordon[a]; Saul Goldman[a]
[a] Guelph-Waterloo Centre for Graduate Work in Chemistry, Ontario, Canada

To cite this Article Gordon, Heather L. and Goldman, Saul(1989) 'The Glassy Wall Boundary for Simulations of Inhomogeneous Systems', Molecular Simulation, 3: 5, 315 — 323

To link to this Article: DOI: 10.1080/08927028908031383

URL: http://dx.doi.org/10.1080/08927028908031383

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Molecular Simulation, 1989, Vol. 3, pp. 315–323
Reprints available directly from the publisher
Photocopying permitted by license only

THE GLASSY WALL BOUNDARY FOR SIMULATIONS OF INHOMOGENEOUS SYSTEMS

HEATHER L. GORDON and SAUL GOLDMAN

Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Guelph, Ontario, Canada, N1G 2W1

(*Received January 1989, accepted March 1989*)

For simulations on systems that invlove a physical inhomogeneity at infinite dilution, the usual periodic boundary conditions are inappropriate. In previous studies on such systems, surfaces have been re-introduced in order to contain the particles of the sample. When smooth surfaces are used to contain liquids, undesirable structural artifacts in the liquid are promoted by these surfaces. In this study a rigid but structurally liquid-like containing surface, that we call a glassy wall boundary, is introduced, in an attempt to solve this problem. It serves as a containing surface, but "looks" nearly liquid-like to molecules in the mobile liquid near it. We illustrate the properties of this boundary for a system that consists of an isolated polyion surrounded by SPC water at 300 K and $\sim 1\,\mathrm{gcm}^{-3}$. We show that this boundary reduces or eliminates some of the problems caused by a smooth surface.

KEY WORDS: simulations, glassy wall boundary, inhomogeneous systems

INTRODUCTION

Computer simulations of homogeneous systems commonly use periodic boundary conditions in order to avoid surface effects [1]. However, for simulations on solutions that are inhomogeneous, with the inhomogeneity present at infinite dilution, periodic boundary conditions are inappropriate, for at least one of the coordinate directions. Examples of such solutions include those containing charged or uncharged surfaces [2–5], those with solutes at infinite dilution [6], *et cetera*. Periodic boundary conditions are inappropriate in these instances, because their use violates the physical requirement of infinite dilution. In some previous studies [2, 3, 7, 8] a surface, in the form of a containing (reflecting) wall, was re-introduced to overcome this problem. Of course this re-introduces surface effects, which, for high density systems like liquids, creates undesirable artifacts. For example, the radial and angular distributions found for water-like liquids near such surfaces are very different from what obtains in the bulk [2–4]. Also, these artifacts can propagate inwards from the wall to some degree [2, 4].

In this paper, we present a new boundary which serves as a containing surface yet has a less deleterious effect on the radial and angular distribution functions of a water-like molecular solvent than does a smooth wall.

SYSTEM AND THEORY

The inhomogeneous system in which we are interested is that of an infinitely long, soft, rigid (unbendable), high charge-density polyion surrounded by a molecular solvent under conditions of infinite dilution. To date, all theoretical and simulation studies of such polyelectrolyte solutions [7, 8] have used the "primitive" electrolyte model [9, 10], wherein the solvent is modelled as a dielectric continuum. In Monte Carlo simulations of such a system [7, 8], the small (mobile) ions are contained within the simulation cell by a smooth, cylindrical wall situated at some large radial distance R_0 from the polyion axis. Periodic boundary conditions are used in the axial direction. Since the ion density turns out to be very low at R_0, this artificial surface does not significantly alter the resulting ion distributions.

We are carrying out a Monte Carlo simulation for the counterion-polyion distribution function in which the dielectric continuum is replaced by a molecular model for the solvent. For a molecular solvent, the containing surface at R_0 must be placed at much shorter distances than those used in continuum studies, in order to keep the number of particles within a practical range (< 2000). However, the solvent structure adjacent to a smooth wall at R_0 will be totally unlike that in the bulk of the solution. Moreover, the structure created by a smooth wall will propagate inwards, due to the long-range electrostatic interactions of the solvent. We have therefore developed, a "glassy wall" to be used at R_0, which more closely approximates a homogeneous solvent environment in the radial direction, and does not promote the artificial radial or angular structure found when a smooth wall is used.

We have examined the structure of SPC water [11], around a polyion, using both smooth and glassy walls at R_0. Periodic boundary conditions are used in the axial direction. The glassy wall is a cylindrical annulus, concentric with the polyion, composed of immobile SPC particles. These SPC particles were mathematically carved out from a homogeneous SPC liquid at the desired temperature and density. The selected particles were those situated within the coordinates of the desired annulus. The positions and orientations of the selected particles were permanently fixed. Mobile SPC molecules surrounding the polyion are thus contained in the radial direction of the simulation cell by a cylindrical wall of SPC water frozen in a configuration typical of that found in the bulk. Hence the term "glassy wall".

Monte Carlo simulations were performed on the pure mobile solvent, both in the presence and absence of an axial charge on the polyion. The extent of polarization of the mobile solvent in the case of the fully charged polyion (without the screening which would normally be provided by the neutralizing ions in solution) is physically unrealistic. However, our purpose here is to investigate the effect of the different constraining walls on solvent structure. The calculations with and without the axial charge, involve degrees of polarization that bracket what would arise in the more realistic screened situation.

CALCULATIONS

i) The Systems

We carried out Monte Carlo simulations using two cylindrical simulation cells. Both cells had an axial height of 25.5 Å. Both contained a rigid, soft, cylindrical polyion whose axis coincided with the axis of the simulation cell. In each case the polyion was surrounded by SPC water. As mentioned previously, the usual periodic boundary conditions were applied in the axial direction.

The total potential energy U_i of the i'th mobile SPC water particle is given by

$$U_i = u_{ip}(r_{ip}) + \sum_{\substack{j \neq i \\ r_{ij} \leqslant R_c}} u_{ij}(r_{ij}) \tag{1}$$

The first term in equation (1) represents the SPC-polyion interaction energy and the second term is the contribution of the SPC interparticle interactions to the potential energy of particle i. The usual SPC–SPC potential [11] is used and a spherical cutoff is applied (in the second term only) if the center of mass separation r_{ij} is greater than R_c. Here R_c is $2.94\,\sigma$, where σ is the SPC molecular diameter, equal to 3.166 Å. When the glassy wall is used, the second term includes the interaction of particle i with immobilized SPC particles in the glassy wall. When the smooth wall is used, $U_i = \infty$ when $r_{ip} \geqslant 25$ Å.

The SPC-polyion interaction for an SPC particle whose center of mass is at radial distance r_{ip} from the axis of the polyion, is given by a sum of Lennard Jones [12] and electrostatic components:

$$u_{ip}(r_{ip}) = u_{ip}^{LJ}(\varepsilon_{ip}, \sigma_{ip}, r_{ip}) + u_{ip}^{el}(r_{ip}) \tag{2}$$

The values of the Lennard Jones parameters ε_{ip} and σ_{ip} were 18.526×10^{-16} erg and 11.583×10^{-8} cm, respectively [13]. The electrostatic component $u_{ip}^{el}(r_{ip})$ is set equal to zero for the uncharged polyion cases.

For an infinitely long polyion with uniform axial charge density $-e/b$, $u_{ip}^{el}(r_{ip})$ is given by [7, 8, 14]

$$u_{ip}^{el}(r_{ip}) = \frac{2e}{b} \sum_{\alpha} q_\alpha \log_e(r_{ip}^{(\alpha)}) \tag{3}$$

In equation (3), q_α is the α'th charge on the i'th SPC particle, $r_{ip}^{(\alpha)}$ is the radial distance between charge α and the axis of the polyion, e is the electronic charge, and b is a distance parameter selected to make $-e/b$ characteristic of double-stranded DNA in water. Thus b was taken as 1.7 Å [7, 8, 14].

The particles for the glassy wall were mathematically carved out from a large, homogeneous sample of SPC water, extensively pre-equilibrated at a density of $1\ \mathrm{gcm}^{-3}$, and a temperature of 300 K, using Monte Carlo simulations and the usual periodic boundary conditions in all directions. A randomly selected configuration was picked from this simulation to create the glassy wall. The 1465 SPC particles selected for the glassy wall were those whose centers fell within a cylindrical annulus having an inner radius of 25 Å, a thickness of $3\,\sigma$, and a height of 25.5 Å. This particular thickness of the glassy wall ensured that a mobile SPC particle next to it was completely surrounded by a sphere of mobile and frozen SPC particles. A thinner glassy wall would have resulted in an asymmetrical environment around these distant mobile SPC's due to spherical cutoff.

ii) Monte Carlo Simulations

All of the Monte Carlo simulations described below employed the force and torque biasing algorithm [15, 16] with the biasing partially turned on ($\lambda = 0.5$). The magnitudes of the maximum translational and rotational step sizes were adjusted so that the average acceptance rate was in the range 0.5–0.6.

Verlet neighbour lists [17], with a list sphere radius of $3.5\,\sigma$, were found to enhance the speed of the simulations by about 36% for the smooth wall and about 60% for

Table 1 Details of Monte Carlo Simulations[(a)]

Type of wall:	*Smooth Wall*[(b)]			*Glassy Wall*[(c)]		
Number of mobile SPC particles	*1450*			*1469*		
Polyion charge[(d)]	*OFF*	*ON*		*OFF*	*ON*	
		(i)[(e)]	(ii)[(f)]		(i)[(e)]	(ii)[(f)]
Equilibration Run (# MC trial steps)	3.0×10^6	5.5×10^6	4.2×10^6	4.2×10^6	6.7×10^6	5.4×10^6
Data Collection Run (# MC trial steps)	5.2×10^6	5.8×10^6	4.4×10^6	6.0×10^6	6.3×10^6	4.8×10^6

(a) All runs are for 300 K.
(b) $U_i = \infty$ in equation (1) if $r_{ip} \geq 25$ Å.
(c) Described in text.
(d) If "OFF", $u_{ip}^{el}(r_{ip}) = 0$ in equation (2). If "ON", $u_{ip}^{el}(r_{ip})$ is obtained by equation (3).
(e) Equilibration run started from a configuration obtained by pre-equilibrating at 300 K.
(f) Equilibration run started from a configuration obtained by pre-equilibrating at 1500 K for ~ 1.0×10^6 steps (see text).

the glassy wall. A trial step with the glassy wall took about 1.2 times as long as one with the smooth wall. The glassy wall calculations required about 1.7 times as much memory as did the one's with the smooth wall.

Simulations were performed on the uncharged and charged polyion at 300 K surrounded by (1) 1450 mobile SPC's contained by a smooth wall situated so that it prevented SPC particles from travelling beyond 25 Å and (2) 1469 mobile SPC's contained by the glassy wall described in the previous section. Thus, the glassy wall was at approximately the same distance from the polyion axis as the smooth wall. Additional simulation details are given in Table 1. The larger number of mobile SPC's used with the glassy wall includes the roughly 19 mobile molecules which partially penetrated the glassy wall when the polyion was uncharged. The use of 1469 mobile SPC's with the glassy wall gave about the same number of mobile SPC's up to 25 Å as using 1450 mobile SPC's with the smooth wall.

In each case, the total potential energy was monitored during an initial equilibration step. When it started to oscillate about a mean value, the system was presumed to be sufficiently equilibrated. Data were then collected over $\sim 5 \times 10^6$ trial steps (Table 1). In the case of the charged polyion with both types of walls, a supplementary check ensured that configuration space had been adequately sampled. Specifically, the temperature was raised to 1500 K for about 1.0×10^6 trial steps. Then the temperature was lowered back to 300 K and equilibration was continued at this temperature. Comparisons were then made between the data collected before and after the 1500 K run. The total energies were found to be statistically the same (i.e. within 0.1%).

RESULTS

The structural data which was collected from the simulations consisted of 1) the singlet radial distribution function $g^{(1)}(r_{ip})$ for the centers of the mobile SPC particles as a function of radial distance from the polyion axis, and 2) distribution functions for the angles between the vector normal to the polyion surface (pointing towards the constraining wall) and the vectors of the molecular dipole μ and of the OH bonds. The latter two orientational distribution functions are designated $P_\mu(\theta)$ and $P_{OH}(\theta)$, respectively. They were obtained by [2]:

$$P(\theta_i) = \frac{N(\theta_i)}{\Sigma N(\theta_i)} \times \frac{1}{(\sin\theta_i)\Delta\theta_i} \tag{4}$$

The distribution functions $P_\mu(\theta)$ and $P_{OH}(\theta)$ should have constant values of 0.5 and 1.0, respectively, for a system displaying no angular anisotropy such as the bulk homogeneous liquid.

$g^{(1)}(r_{ip})$ was normalized using a bulk density of 1 gcm^{-3}. $P_\mu(\theta)$ and $P_{OH}(\theta)$ were normalized to a constant solid angle by the factor $1/\sin\theta$, as in references [2, 4].

The orientational structure of water-like solvents next to smooth, hydrophobic surfaces has been discussed previously by others [2, 4]. We are interested in determining the extent to which the glassy wall used in this simulation diminishes the artifacts that smooth surfaces create. The relevant results are shown in Figures 1 and 2 and in Table 2.

The results we present are for the angular functions $P_\mu(\theta)$ and $P_{OH}(\theta)$ with the

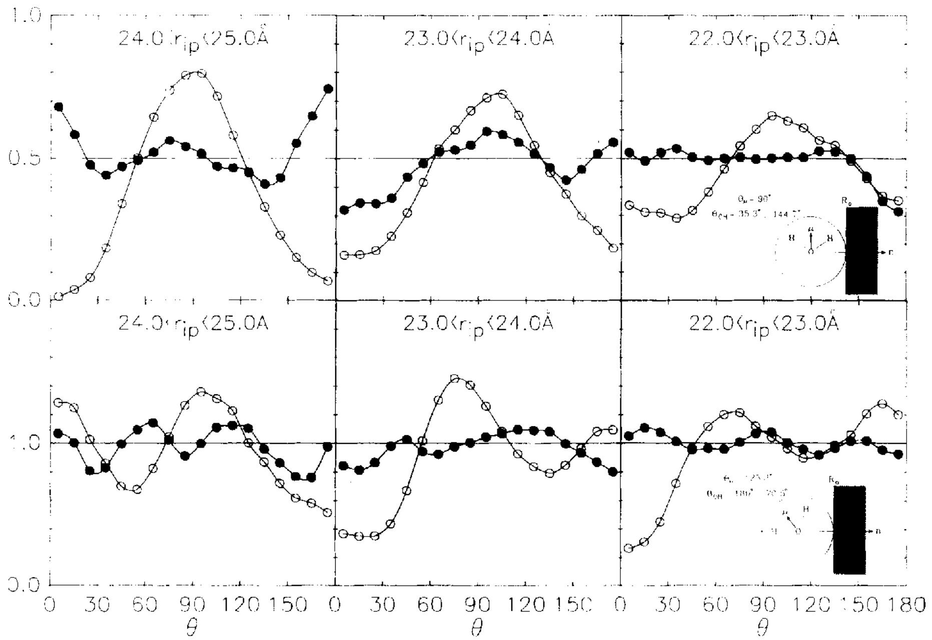


Figure 1 Angular distribution functions for the uncharged polyion that characterize the average orientation of SPC water molecules near two cylindrical containing walls. The functions are defined by equation (4); $\Delta\theta = 10°$. Legend: (○) smooth wall; (●) glassy wall. In a homogeneous fluid, $P_\mu(\theta) = 0.5$ and $P_{OH}(\theta) = 1.0$ at all θ. The insets illustrate the meaning of θ.

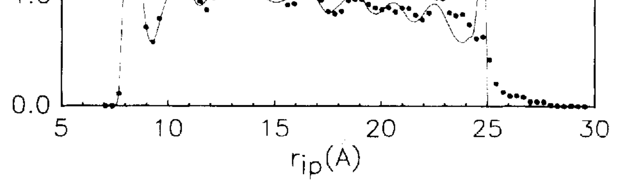


Figure 2 The singlet SPC water distribution function as a function of distance from the polyion axis for the charged polyion. $\varrho g^{(1)}(r_{ip})$, where ϱ is the bulk density, is the microscopic average density of SPC particles at a distance r_{ip} from the polyion axis. Legend: (—) smooth wall; (●) glassy wall. Smooth and glassy walls are situated as described in Footnote (a), Table 2. The results are for an annular thickness of 0.1 Å.

Table 2 Root-Mean-Squared Deviation from the homogeneous (limiting) values: $P_\mu(\theta) = 0.5$ and $P_{OH}(\theta) = 1.0$

Distance from the Polyion Axis[(a)] *(Å)*	*Type of wall*[(b)]	*Function*[(c)]	
		$P_\mu(\theta)$	$P_{OH}(\theta)$
22–23	glassy	0.0598	0.0671
	smooth	0.130	0.308
23–24	glassy	0.0884	0.100
	smooth	0.212	0.360
24–25	glassy	0.0915	0.125
	smooth	0.300	0.278

(a) The smooth wall is situated so that no SPC center penetrates beyond a radial distance of 25 Å from the polyion axis; the glassy wall is at approximately 25 Å from the polyion axis (see text).

(b) The smooth wall is a cylindrical reflecting surface; the glassy wall consists of immobilized liquid-like SPC particles. Both act as containing surfaces in the radial direction (see text).

(c) These functions are defined by equation (4) and are displayed in Figure 1. The entries here were obtained from the points shown in Figure 1.

uncharged polyion and the radial $g^{(1)}(r_{ip})$ function with the charged polyion. With the charged polyion, the angular functions displayed a saturation effect, in that the field of the polyion almost entirely swamped out any differences in these functions caused by the two types of walls. With the uncharged polyion, the singlet distribution functions $g^{(1)}(r_{ip})$ showed little or no difference next to the two different walls.

It is clear from Figure 1 and Table 2 that, for the uncharged polyion, the angular distribution functions $P_\mu(\theta)$ and $P_{OH}(\theta)$ are both more "bulk-like" near the glassy wall than near the smooth wall. Figure 1 confirms that the smooth wall creates significant anisotropic distortions in $P_\mu(\theta)$ and $P_{OH}(\theta)$ that propagate for some distance into the solution. While the glassy wall results are not entirely free of distortion, they are clearly much more nearly so than the smooth wall results. This point is made strikingly clear by the entries in Table 2, from which it is seen that in every instance the glassy wall's distorting influence is significantly less than that due to the smooth wall. The peak at 25 Å in Figure 2 indicates that the smooth (inert) wall seems to be wetted by SPC water when the central polyion is charged. While this result is interesting in its own right, it is an undesirable artifact in the present context. This artifact is seen to be entirely eliminated by the use of the glassy wall.

From Figure 2, it is seen that there is an undesirable asymmetry in the solvent concentration for both smooth and glassy wall simulations when the polyion charge is turned on. Specifically, in the range $17\,\text{Å} \leqslant r_{ip} \leqslant 25\,\text{Å}$, the water density gradually diminishes with increasing r_{ip}. This is due to electrostriction of the water caused by the unscreened, and therefore very high, electric field of the polyion. We know that this is the source of the density drift, because it did not occur in our (unpublished) calculations where the polyion charge was turned off. In more realistic scenarios, screening by the counterions will mitigate this effect. There are also techniques for avoiding this asymmetry such as the use of much larger systems, constant (T, V, μ) Monte Carlo, or the addition of extra solvent particles to the system to offset the density depletion in the "bulk" (17 Å–25 Å here). Each of these solutions has a drawback: much larger systems would require too much computer time, (T, V, μ) simulations are not feasible at liquid water densities, and the addition of extra particles is *ad hoc* (i.e. how many extra particles are appropriate?). Fortunately, screening by counterions would, in reality, reduce or eliminate the need for any of these remedies.

CONCLUSIONS

We expect that the degree of radial and orientational solvent structure near a constraining wall for a charged polyion together with its neutralizing counterions will be intermediate between the charged and uncharged polyion results. This is because the field of the polyion charge will be partially screened by the counterions. The use of a glassy wall rather than a smooth wall is strongly indicated for this (more realistic) problem by the foregoing results. Extensions of the glassy wall idea to other systems, such as those mentioned in the Introduction, is straightforward. The glassy wall should be especially useful in simulations on the electrical double layer when these are done using a molecular model for the solvent.

Acknowledgements

We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial assistance and to the University of Guelph for its continuing support of the Special Computing Program and the Array Processor. It is also a pleasure to thank Dr. Uwe Oehler for preparing the insets in Figure 1.

References

[1] J.P. Valleau and S.G. Whittington, "A Guide to Monte Carlo for Statistical Mechanics: 1. Highways," in *Statistical Mechanics, Part A: Equilibrium Techniques*, B.J. Berne, ed., Plenum Press, New York (1979).

[2] C.Y. Lee, J.A. McCammon and P.J. Rossky, "The structure of liquid water at an extended hydrophobic surface," *J. Chem. Phys.*, **80**, 4448 (1984).

[3] J.P. Valleau and A.A. Gardner, "Water-like particles at surfaces. I. The uncharged, unpolarized surface," *J. Chem. Phys.*, **86**, 4162 (1987).

[4] G.M. Torrie, P.G. Kusalik and G.N. Patey, "Molecular solvent model for an electrical double layer: Reference hypernetted-chain (RHNC) results for solvent structure at a charged surface," *J. Chem Phys.*, **88**, 7826 (1988).

[5] G.M. Torrie, P.G. Kusalik and G.N. Patey, "Molecular solvent model for an electrical double layer: Reference hypernetted-chain (RHNC) results for ion behavior at infinite dilution," *J. Chem. Phys.*, **89**, 3285 (1988).

[6] S. Goldman and P. Backx, "One water's ability to dissociate ion pairs," *J. Chem. Phys.*, **84**, 2761 (1986).

[7] P. Mills, C.F. Anderson and M.T. Record, Jr., "Monte Carlo Studies of Counterion-DNA Interactions. Comparison of the Radial Distribution of Counterions with Predictions of Other Polyelectrolyte Theories," *J. Phys. Chem.*, **89**, 3984 (1985).

[8] C.S. Murthy, R.J. Bacquet and P.J. Rossky, "Ionic Distributions near Polyelectrolytes. A Comparison of Theoretical Approaches," *J. Phys. Chem.*, **89**, 701 (1985).

[9] W.G. McMillan and J.E. Mayer, "The statistical thermodynamics of multicomponent systems," *J. Chem. Phys.*, **13**, 276 (1945).

[10] H.L. Friedman and W.D.T. Dale, "Electrolyte Solutions at Equilibrium," in *Statistical Mechanics. Part A: Equilibrium Techniques*, B.J. Berne, ed., Plenum Press, New York (1979).

[11] H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren and J. Hermans, "Interaction models for water in relation to protein hydration," in *Intermolecular Forces*, B. Pullman, ed., Reidel, Dordrecht, 1981.

[12] The Lennard-Jones pair potential is defined by:

$$u^{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

where ε is the well-depth and σ is the distance at which $u^{LJ}(r) = 0$.

[13] From $\sigma_{ip} = (\sigma + \sigma_{pp})/2$, with $\sigma = 3.166$ Å (the value for SPC water) and $\sigma_{pp} = 20$ Å. The latter

value and that for ε_{ip} were chosen so that the minimum in the isolated SPC-polyion potential (when the SPC dipole points straight towards the polyion axis) fell at 9 Å. This causes the Lennard Jones core of the polyion to have roughly the same diameter and softness as used previously [see references 7, 8, 14].

[14] H. Gordon and S. Goldman, "Simulations on the Primitive Electrolyte Environment of a High Charge-Density Polyeletrolyte. A Sampling Problem and its Solution," *Molecular Simulation*, accepted (1988).

[15] M. Rao, C. Pangali and B.J. Berne, "On the force bias Monte Carlo simulation of water: methodology, optimization and comparison with Molecular Dynamics," *Mol. Phys.*, **37**, 1773 (1979).

[16] S. Goldman, "A simple new way to help speed up Monte Carlo convergence rates: Energy-scaled displacement Monte Carlo," *J. Chem. Phys.*, **79**, 3938 (1983). Appendix.

[17] M.P. Allen and D.J. Tildesley, *Computer Simulation of Liquids*, Clarendon Press, Oxford (1987). Section 5.3.1.