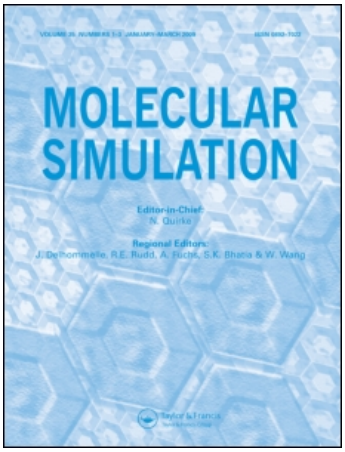

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A 'PARTIALLY CLOTHED' PIVOT ALGORITHM FOR MODEL POLYELECTROLYTE SOLUTIONS

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For the Monte Carlo study of polymer configurations, the "pivot algorithm" has proved very effective for both lattice and continuum models. Its efficiency deteriorates for a polyion immersed in a bath of free ions, however, since to pivot a substantial segment of the polyion without any of its sheath of counterions carries a large energy expense. This article reports an attempt to relieve that problem by including, in pivot moves, a portion of the ion atmosphere. It is shown that this leads to substantial gains, at least for moderately low ionic concentrations, and allows useful estimation of difficult quantities, such as persistence length.

KEY WORDS: Pivot algorithm, polyelectrolytes, Monte Carlo simulations.

1 INTRODUCTION

Computer simulations have made important contributions to the understanding of how electrostatic interactions of a single polyion with the co-ions and counterions of a supporting electrolyte give rise to the characteristic properties of dilute polyelectrolyte solutions [1–11]. Nevertheless there remain discrepancies between various theories of polyelectrolyte solutions, experimental results, and computer simulations [3,4,5,8–10,12–15]. In part, these are due to the over-simplified models to which theory and simulation have been applied. To date, most theories and simulations of polyelectrolyte solutions have employed a rigid rod model for the polyion at infinite dilution [16,17]. The rigid rod model is properly applied to the study of polyions at high linear-charge-density and at low concentrations of supporting electrolyte. For these systems poor screening of strong repulsions along the polyion backbone gives rise to a significantly extended polyion conformation. Theories and simulations using rigid rod models provide descriptions of the distributions of co-ions and counterions about a single conformation of the model polyion. For low-charge-density polyelectrolytes and/or high concentrations of supporting electrolyte, the conformation of the polyion cannot be adequately represented by the rigid rod model. In these cases, flexible polyion models are more suitable [18–46]. However it is quite difficult to do accurate simulations including both flexible polyions and the free ions of the supporting electrolyte. For this reason it has been common to use an approximation in which an

effective intrapolyion potential energy attempts to account for screening of the polyion charges by the supporting electrolyte [18,19,21,22,24,26–29,31–42,44–46]. Due to the considerable computational effort required, only a few studies have attempted to characterize the discrepancies between such a model and a more complete treatment in which the free ions are included along with a flexible polyion [20,23,25,30,43].

We present here a Monte Carlo (MC) sampling algorithm that leads to improved convergence of various polyion conformational properties, for the model of a single flexible polyion where free co-ions and counterions are explicitly included. This algorithm is a variation of the pivot algorithm [47–49]. The idea of the pivot algorithm is to allow large-scale changes in the conformation of a model polymer in a single Monte Carlo step, by pivotting substantial segments of the chain. Such dramatic steps, even if they are not very frequent, can enhance enormously the sampling of the conformations [49].

However a new situation arises if the model includes free counterions and co-ions along with a polyion. This is because a pivot of a substantial segment of the polyion, if it leaves behind the whole of its counterion "sheath", will be very expensive energetically; such moves will rarely occur in a Monte Carlo calculation. Moreover, the counterion atmosphere will have to be entirely re-equilibrated after each such pivot is accepted. Our extension of such a 'bare' polyion pivot involves accompanying the pivotted chain segment by a portion of its ion atmosphere. We show that as a consequence, the acceptance rate and effectiveness of the pivots increase and hence the convergence rate of polyion conformational properties is increased.

2 MODEL

The model used here has been described previously [20]. A 'bead necklace' model is used for the polyion: M hard spheres, each with an embedded point charge, represent the univalent ionizable groups along the polyion backbone. A square well potential constrains adjacent beads to fall between minimum and maximum separations, so that the 'bondlength' b between charged groups is allowed to vary between $S_{min} \leqslant b \leqslant S_{max}$. In the model described here , $S_{min} = 8.0$ Å and $S_{max} = 10.0$ Å. (This intracharge separation corresponds to that of a low-charge-density polyion.) Overlaps between non-adjacent polyion beads are prevented by a hard-sphere potential with an ion diameter of $\sigma = 4.25$ Å. Univalent co-ions and counterions of the supporting electrolyte are modelled as charged hard spheres having the same diameter as the polyion beads. The solvent is described only as a continuum dielectric with a bulk dielectric constant $\varepsilon = 78.5$, representing water at 298.15 K and 1 atmosphere.

A central polyion bead of the chain is fixed at the centre of a sphere, which has a hard boundary at R_{out} acting as a container for the polyion and its 'bath' of co-ions and counterions. Electroneutrality was maintained within the simulation cell: the sum of charges from all counterions present exactly equalled that contributed by all co-ions plus the polyion charges. The radius R_{out} of the spherical simulation cell is chosen to be sufficiently large so that it is well-removed from the polyion and its ionic atmosphere. In all cases, the concentrations of co-ions and counterions were found to be equal within at least 5 debye lengths of R_{out}.

All simulations were performed within a semi-grand-canonical ensemble, in which the number of free ions fluctuated in correspondence with a fixed chemical potential. The Markov chain of the Monte Carlo runs involved five distinct types of moves: (1) small translational moves of an individual polyion bead, (2) translational moves of a free co-ion or counterion, (3) addition of a co-ion/counterion pair of free ions, (4) deletion of such a pair, and (5) pivots of segments of the polyion chain. The first four move types have been described in detail previously [20]. This article concerns optimization of the pivot moves, by the inclusion of some part of the ion atmosphere surrounding the polyion; the details are discussed in the following section.

3 THEORY

Each Monte Carlo Markov chain among the configurational states of the system must have the desired limiting distribution. A sufficient (although not necessary) condition to ensure that the correct limiting distribution is realized is that of microscopic reversibility or detailed balance [50]. If $\pi = \{\pi_i\}$ is the (normalized) equilibrium distribution of the system and $p = \|p_{ij}\|$ is the stochastic matrix of transition probabilities between states characterizing the Markov chain, then the appropriate condition of detailed balance requires that

$$p_{ij}\pi_i = p_{ji}\pi_j \tag{1}$$

for a transition between any two states i and j. In practice, one attempts 'trial' steps from state i to state j with a probability q_{ij}; the trial step is accepted with a probability a_{ij}, leading to an overall transition probability $p_{ij} = q_{ij}a_{ij}$. Then equation (1) becomes

$$\frac{a_{ij}}{a_{ji}} = \frac{q_{ji}\pi_j}{q_{ij}\pi_i} \tag{2}$$

Equation (2) prescribes whether an attempted transition between states i and j is accepted, given the ratio of π_j/π_i (defined by the chosen ensemble) and q_{ji}/q_{ij} (defined by the 'trial' transition matrix $\|q_{ij}\|$).

The pivot algorithm, as initially described by Lal [47], was developed with lattice models of polymers in mind. Although this sampling algorithm was often dismissed out-of-hand as being inefficient in the early years after its inception, the pivot algorithm's superior convergence-properties were firmly established by Madras and Sokol [49]. Since then there have been various applications [51, 52] and the pivot algorithm has also been applied to off-lattice (continuum) polymer configurations [56, 57].

We are interested in the more complicated situation of sampling the configurations of a model polyion in the presence of free counterions and co-ions. We compare, in what follows, pivots of 'bare' segments of the polyion chain with those of segments 'partially clothed' by their adjacent free ions. In the former case, the trial step is chosen in the following way: one bead of chain, M_{pivot}, is chosen at random. The shorter end of the chain is then pivotted through a random angle $\Theta(-\pi < \Theta \leqslant \pi)$

about a randomly oriented axis through M_{pivot}. If M_{pivot}, Θ, and the axis of rotation are all chosen from uniform distributions, then the 'trial' transition matrix is symmetrical: $q_{ij} = q_{ji}$. To sample on the Boltzmann distribution, equation (2) can then be satisfied by

$$a_{ij} = \min(1, \exp\{-\beta(u_j - u_i)\}), \tag{3}$$

where u_i is the potential energy of the state i, and $\beta = 1/k_B T$, k_B being Boltzmann's constant and T the temperature.

Table 1 lists the percentage of accepted pivots of 'bare' chain segments for polyions of lengths $M = 10, 20$, and 50 and supporting electrolyte concentrations of approximately 0.001, 0.01, 0.1, and 1.0 mol/dm^3. Pivot moves are rejected more frequently both as the length of the polyion chain and concentration of supporting electrolyte increases. A pivot move will be rejected if ions of the pivotted chain segment overlap with ions of

Table 1 Acceptance and rejection rates for 'bare' pivots of polyions of various lengths and concentrations of supporting electrolyte[a]

System[c]	%Pivots Accepted[b]	%Pivots Rejected[b]	
		Overlaps[d]	Boltzmann[e]
0.0010 mol/dm^3			
M			
10	63.7%	6.9%	29.4%
20	46.5%	9.0%	44.6%
50	23.3%	12.0%	64.8%
0.011(6) mol/dm^3			
M			
10	58.3%	10.8%	30.9%
20	38.0%	15.7%	46.4%
50	17.3%	23.6%	59.2%
0.10 mol/dm^3			
M			
10	47.3%	20.2%	32.5%
20	27.7%	31.2%	41.1%
50	11.9%	51.0%	37.1%
1.0 mol/dm^3			
M			
10	22.9%	59.9%	17.2%
20	11.8%	77.5%	10.6%

[a] Determined from Monte Carlo simulations using model described in text.

[b] As a percentage of total number of pivots.

[c] M is the number of charges along polyion chain. Concentration is that of supporting electrolyte.

[d] Percentage of pivots rejected due to overlaps of the pivotted chain with unpivotted chain and/or ions of the supporting electrolyte.

[e] Percentage of pivots rejected by the Boltzman test, equation (3).

the unpivotted portion of the polyion and/or with bath ions. If overlaps do not occur, and if the configurational energy of the trial step is unfavourable, application of equation (3) results in rejection of the pivot with the prescribed probability. Table 1 also lists the percentages of rejected moves due to overlaps and the Boltzmann test. For the three lowest electrolyte concentrations, a large proportion of the pivots are rejected due to energetic considerations, and it is here that it may be possible to increase the numbers of pivots accepted by including counterions in the pivot and thus generating trial configurations with lower energies. Since more than 60% of pivot rejections at 1.0 mol/dm^3 are due to overlaps, benefits from an improvement in the acceptance/rejection ratio due to pivotting ions along with the chain segment will likely be outweighed by these overlap rejections.

One might consider pivotting, along with the selected chain segment, *all* of the bath ions that fall within some pre-determined radius R_{pivot} of any of the pivotted chain ions. Label the starting configuration i and let m_i represent these free ions that are to be pivotted along with the polyion segment. The trial pivot then leads to a configuration j that will have, within R_{pivot} of the new coordinates of the (pivotted) chain ions, not only the m_i pivotted bath ions, but also any non-pivotted counterions and co-ions whose original unchanged positions lie within this volume. Let m_j represent the *sum total* of the free ions falling within R_{pivot} of the coordinates of the pivotted chain ions in configuration j. It is clear that $m_j \geqslant m_i$. If $m_j = m_i$, initial configuration i is accessible from state j ($q_{ji} > 0$). But state i is inaccessible from configuration j if $m_j > m_i$, since there exists no pivot of the chain segment plus its *entire sheath* of m_j bath ions that will reproduce configuration i. Therefore, when a pivot move leads to a configuration with $m_j > m_i$, equation (2) must be satisfied by rejecting the trial move, i.e. by setting the acceptance probability $a_{ij} = 0$. Given that many attempted pivots are likely to be rejected for this reason, pivotting of *all* eligible bath ions may not achieve our goal of increasing the pivot acceptance rate. A generalization of this selection process, which may improve sampling efficiency, instead chooses for inclusion in the pivot each of the m_i bath ions with some probability $P_{\text{pivot}} < 1$.

In this case, each of the m_i ions is included in the trial step with a probability $P_{\text{pivot}} < 1$: a subset m_i^p of all the m_i bath ions that fall within R_{pivot} of the selected polyion segment is pivotted; $m_i^p \leqslant m_i$. The remaining $(m_i - m_i^p)$ bath ions are not pivotted but remain in their original positions. Following the argument in the above paragraph, configuration i is accessible from configuration j *only* when the subset m_j^p, selected for pivotting from all eligible m_j bath ions of state j, is *identical* to the original subset m_i^p. Any additional $(m_j - m_i^p)$ ions are left behind. The ratio of the 'trial' transition probabilities for the forward and reverse pivots is then

$$\frac{q_{ij}}{q_{ji}} = \frac{(P_{\text{pivot}})m_i^p(1 - P_{\text{pivot}})^{(m_i - m_i^p)}}{(P_{\text{pivot}})m_i^p(1 - P_{\text{pivot}})^{(m_j - m_i^p)}} \tag{4}$$

Thus equation (2) is satisfied by:

$$a_{ij} = \min\{1, (1 - P_{\text{pivot}})^{(m_j - m_i)} \exp\{-\beta(u_j - u_i)\}\} \tag{5}$$

4 SIMULATIONS

Results for Monte Carlo simulations that pivotted the 'bare' polyion chain were compared to those where the pivotted chain segment was accompanied by a portion of its ion atmosphere. We shall designate the latter type of pivot as 'partially clothed'. Table 2 contains values of parameters used for four independent simulation runs of a flexible polyion of 50 singly-charged monomers ($M = 50$) along with acceptance probabilities for the various types of moves. Columns 1 and 2 describe, respectively, simulations that employed 'bare' and 'partially clothed' pivots; both were performed at a supporting electrolyte concentration of 0.0116 mol/dm^3. 'Bare' and 'partially clothed' pivot algorithms were also used in the other two simulations, but at a higher electrolyte concentration of 0.100 mol/dm^3 (columns 3 and 4). 'Partially clothed' pivots selected ions within the volume defined by $R_{\text{pivot}} = 2\sigma$ with a probability $P_{\text{pivot}} = 0.5$. We did not discriminate between co-ions and counterions when selecting bath ions for a pivot move.

Data for both simulations at 0.0116 mol/dm^3 were collected for 24×10^6 MC steps after a suitable pre-equilibration period. For the 0.100 mol/dm^3 simulations, data were collected for 48×10^6 steps and 36×10^6 steps where respectively 'bare' pivots and 'partially clothed' pivots were employed, again after an appropriate pre-equilibration period.

5 RESULTS

Results are reported in Table 3 and Figures 1–8.

Acceptance rates for the five types of trial moves are given in Table 2. Pivotting ions along with the polyion chain does increase the percentage of pivots accepted: for the 0.0116 mol/dm^3 system, there was a 17.2% acceptance rate for 'bare' pivot moves, whereas the acceptance rate for 'partially clothed' pivots was 22.4%. At the higher concentration of 0.100 mol/dm^3, the acceptance rate was 11.9% for pivots of polyion segments only, but this increased to 15.3% when ions were included in the pivot. This improvement sounds very modest. However Figure 1 shows (and it might be expected) that it is especially for pivots of the longer chain segments that the frequency of acceptances is substantially increased when 'partially clothed' pivots are used; as we will demonstrate later, these are key for improving the sampling. Rejections due to overlaps for the 0.0116 mol/dm^3 simulations account for 23.3% of all pivot moves where 'bare' pivots were used and for 'partially clothed' pivots, 21.3%. For the 0.100 mol/dm^3 systems, the corresponding values are 51.0% and 51.1% for 'bare' and 'partially clothed' pivot simulations. Therefore the increase in the percentage of pivots accepted when bath ions are pivotted is indeed due to an improved Boltzmann acceptance/rejection ratio and not because fewer overlaps occur. The average number of ions pivotted along with each chain segment is not large: overall, only 0.8 bath ions were moved during an accepted pivot step for the 0.0116 mol/dm^3 simulation and 1.4 bath ions at 0.100 mol/dm^3.

Although the increase in accepted chain pivots from 17.2% to 22.4% or 11.9% to 15.3% is not dramatic, it produces significantly better convergence rates for global

Table 2 Parameters for semi-Grand Canonical Monte Carlo Simulations[a]

	Simulations			
Parameters	*'Bare' pivots*	*'Partially clothed' pivots*	*'Bare' pivots*	*'Partially clothed' pivots*
Supporting electrolyte concentration(mol/dm^3)	0.0116		0.100	
R_{out}[b](Å)	300		170	
R_{in}[c](Å)	150		145	
p_{bin}[d]	0.5		0.8	
p_{bout}[e]	0.5		0.2	
$\Delta_{polyion}$; $\Delta_{bath\ ion}$[f]	0.25σ; 15σ		0.25σ; 5σ	
P_{pivot}; R_{pivot}[g]	—	0.5; 2σ	—	0.5; 2σ
Configurations in run[h]	24 × 10^6[i]		48 × 10^6[j]	36 × 10^6[j]
Proportion of move types[k]				
$f_{(1)}$:$f_{(2)}$:$f_{(3)}$:	0.2:0.2:0.2:		0.2:0.2:0.2:	
$f_{(4)}$:$f_{(5)}$	0.2:0.2		0.2:0.2	
Acceptance Rates:				
Translations of chain ions	52.6%		51.5%	51.6%
Translations of bath ions	62.1%	62.0%	66.2%	66.1%
Additions of ion pairs	71.5%		59.6%	59.7%
Deletions of ion pairs	71.4%		59.7%	
Pivots	17.2%	22.4%	11.9%	15.3%

[a] Parameters as described in sections 2, 3, 4 and reference [20].

[b] Radius of hard outer boundary of spherical container.

[c] Radius of inner sampling sphere; $R_{in} \leqslant R_{out}$. Preferential sampling of counterions and co-ions (for both translational moves and ion pair additions/deletions) was performed inside the volume defined by R_{in} (see references [20] and [58]).

[d] Relative probability of sampling bath ion moves (translational, ion pair additions and ion pair deletions) inside the inner sampling sphere (see references [20] and [58]).

[e] Relative probability of sampling bath ion moves (translational, ion pair additions and ion pair deletions) outside the inner sampling sphere (see reference [20] and [58]).

[f] Maximum step size in each cartesian direction for translational moves of polyion beads and bath ions, respectively. $\sigma = 4.25$ Å.

[g] P_{pivot} is the probability that a bath ion, which falls within R_{pivot} of any pivotted polyion bead, will also be selected for the pivot move. $\sigma = 4.25$ Å. This value of R_{pivot} was found to give the maximum percentage of pivots accepted among a series of five short (40,000 MC steps for 0.0116 mol/dm^3 and 80, 000 MC steps for 0.100 mol/dm^3) simulation runs for which $P_{pivots} = 0.5$ and R_{pivots} was set to 0σ, 1.5σ, 2.0σ. 2.5σ, and 3.0σ.

[h] Number of MC steps over which data were collected.

[i] The initial configuration for both these simulations was the same equilibrated conformation. This was taken as the last configuration of a long simulation (24 × 10^6 MC steps) that used identical sampling as for the runs over which data were collected except for a minor modification in translational moves of the free ions.

[j] These two simulations did not have the same starting configuration. A random initial configuration for both polyion and bath ions was used for the simulation that employed 'bare' polyion pivots, and the system was pre-equilibrated for 4 × 10^6 MC steps. The final conformation of the subsequent collection run was taken as the initial configuration for the simulation that used 'partially clothed' pivots.

[k] Move types: (1) Translations of polyion beads; (2) Translations of bath ions; (3) Additions of ion pairs; (4) Deletions of ion pairs; (5) Pivots of chain with/without bath ions.

Table 3 Conformational properties of flexible polyion with $M = 50$ at 0.0116 and 0.100 mol/dm^3 supporting electrolyte as determined by semi-Grand-Canonical Monte Carlo simulations

	Simulations[a]			
	0.0116 mol/dm^3		*0.100 mol/dm^3*	
	'bare'[b] *pivots*	*'partially*[b] *clothed' pivots*	*'bare'*[c] *pivots*	*'partially*[d] *clothed' pivots*
⟨Concentration⟩ (mol/dm^3)	0.01157 (±.00001)	0.01158	0.09779 (±.00004)	0.09772 (±.00003)
$\langle x_{cm}\rangle$(Å)	4.4 (±1.1)	−0.5 (±0.9)	−0.7 (±2.3)	2.2 (±1.4)
$\langle y_{cm}\rangle$(Å)	−2.3 (±1.1)	−1.4 (−0.9)	5.1 (±1.8)	0.8 (±1.4)
$\langle z_{cm}\rangle$(Å)	−2.4 (±1.2)	0.9 (±0.9)	−5.5 (±1.7)	1.8 (±1.3)
$\langle R_g^2\rangle$(Å^2)	3678 (±47)	3719 (±29)	2187 (±69)	2234 (±30)
$\langle L\rangle$(Å)	163.7 (±1.5)	163.8 (±0.8)	117.3 (±2.3)	117.8 (±1.1)
$\langle L_p\rangle$(Å)	39.3 (±2.1)	43.9 (±1.5)	19.2 (±2.6)	26.6 (±1.3)
$\langle b\rangle$(Å)	9.143 (±0.001)	9.145	9.129 (±0.001)	9.128

[a] Simulations as described in text and Table 2.
[b] Standard deviations computed from 150 sub-averages computed from consecutive blocks of 160,000 configurations over the entire collection period.
[c] Standard deviations computed from 50 sub-averages computed from consecutive blocks of 960,000 configurations over the entire collection period.
[d] Standard deviations computed from 90 sub-averages computed from consecutive blocks of 400,000 configurations over the entire collection period.

polyion conformational properties. Table 3 contains values of the MC estimates of the mean square radius of gyration, $\langle R_g^2\rangle$, mean end-to-end length, $\langle L\rangle$, mean components of the instantaneous polyion centre-of-mass, $\langle x_{cm}\rangle$, $\langle y_{cm}\rangle$, $\langle z_{cm}\rangle$, and mean 'persistence' length, $\langle L_p\rangle$, which we define as[1]

$$\langle L_p\rangle = \frac{1}{2}\left\langle \sum_{i=1}^{M/2} b_i \cos(\theta_i)\right\rangle + \frac{1}{2}\left\langle \sum_{i=M/2}^{M-1} b_i \cos(\theta_i)\right\rangle \tag{6}$$

where b_i is the 'bondlength' of the i^{th} polyion segment (as measured between the i^{th} and $(i+1)^{st}$ polyion bead) and θ_i is the angle between the i^{th} segment and the central $(i = M/2)$ segment. Therefore, $\langle L_p\rangle$ is a measure of the local rigidity of the chain, as measured from its centre. Table 3 also includes estimates of the standard deviations computed from subaverages of consecutive blocks of configurations taken over the

[1] Note that equation (6) is slightly different from that used by other workers [21, 35, 46], in that the distances between adjacent polyion beads are not of fixed length and so b_i must fall inside the summation signs. In addition, we have chosen to include, as the entire contribution from the central polyion segment to L_p, $\langle b_{M/2}\cos(\theta_{M/2})\rangle \equiv \langle b_{M/2}\rangle$, rather than half that value, as is more commonly done.

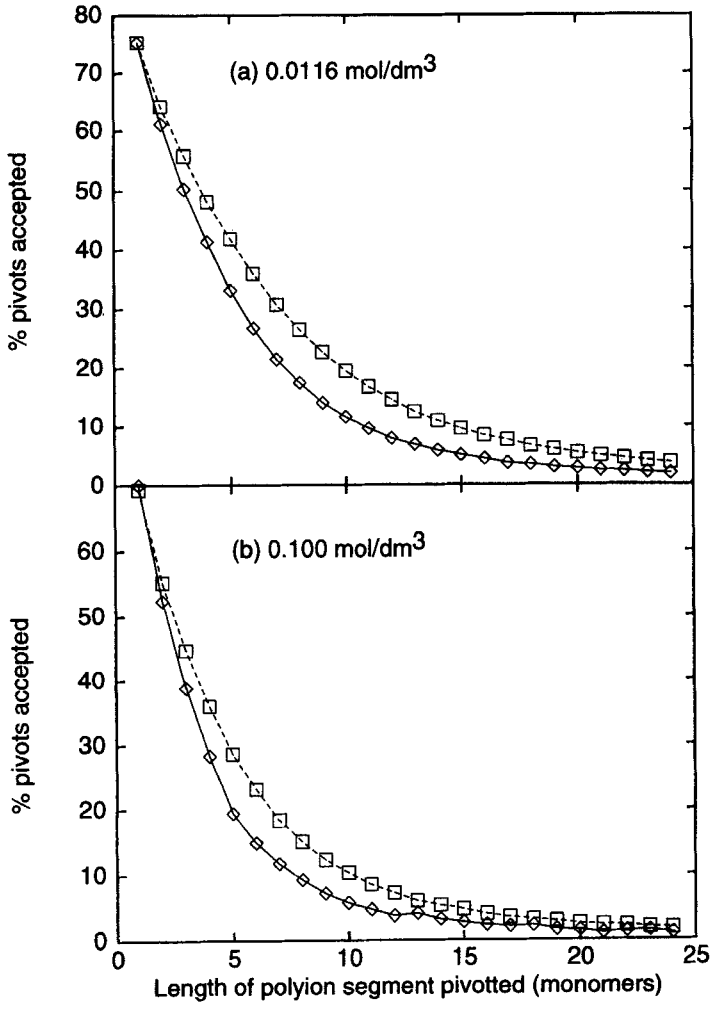

Figure 1 Percentage of pivots accepted as a function of length of polyion segment pivotted (monomer units) for a polyion with $M = 50$: (a) 0.0116 mol/dm^3; (b) 0.100 mol/dm^3. —◇— 'bare' pivots; ---□-- 'partially clothed' pivots.

entire data collection period. The number of configurations comprising each block was found to be sufficiently large so that their estimates of expected values were uncorrelated with each other [59, 60]. The estimates of $\langle R_g^2 \rangle$ and $\langle L \rangle$ from simulations that employ 'partially clothed' polyion pivots fall within one standard deviation of the corresponding estimates from the 'bare' pivot simulations. Therefore the agreement for these two global polyion conformational properties, as found by these two different sampling methods, is good, and reassures us that convergence in both cases has been obtained. However, for $\langle L_p \rangle$ the agreement is not so good: the results from the 'partially clothed' simulations lie above those from the 'bare' pivot simulations, and

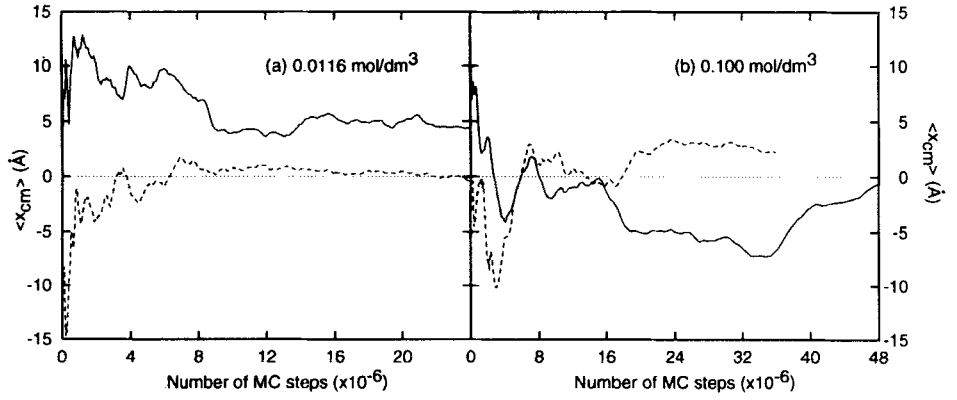

Figure 2 Cumulative average of the x–component (space-fixed-frame) of the polyion centre-of-mass, $\langle x_{cm} \rangle$, as a function of simulation length (number of Monte Carlo steps): (a) 0.0116 mol/dm^3. (b) 0.100 mol/dm^3. —— 'bare' pivots; --- 'partially clothed' pivots.

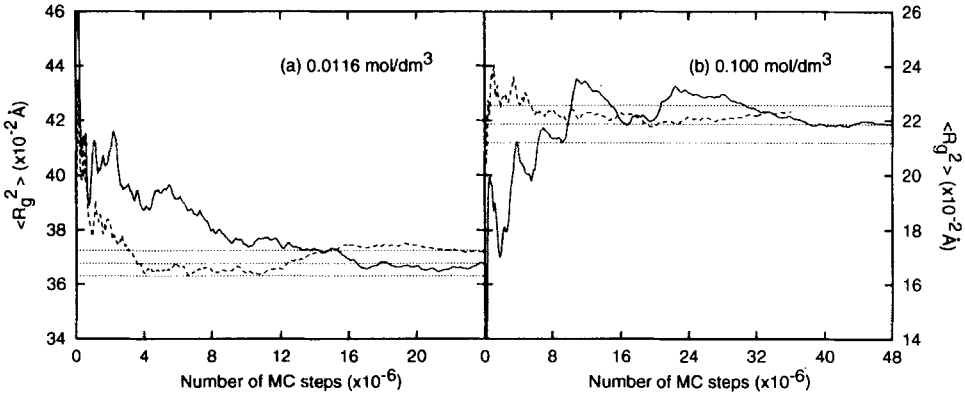

Figure 3 Cumulative average of the polyion mean square radius of gyration, $\langle R_g^2 \rangle$, as a function of simulation length (number of Monte Carlo steps): (a) 0.0116 mol/dm^3; (b) 0.100 mol/dm^3. ——'bare' pivots; – – – 'partially' clothed' pivots; 'dotted lines show' ; $\langle R_g^2 \rangle$ over entire 'bare' pivot simulation ± 1 standard deviation.

sometimes substantially so. (The convergence rates of the persistence length are discussed in more detail later in this section.) The error estimates of these three polyion conformational properties for the results of the 'partially clothed' pivot simulation are always less than those for the 'bare' pivot simulation of the same supporting electrolyte concentration. On the other hand, the convergence of certain local conformational properties, such as the mean bondlength $\langle b \rangle$, is unaffected by the type of pivot algorithm used, since pivots of chain segments leave b_i, $i = 1, M-1$, unchanged. Distributions of counterions and co-ions around the polyion have also been examined (and will be reported elsewhere); those produced by the 'bare' and 'partially clothed' pivot algorithms, given the same supporting electrolyte concentration, are indistinguishable.

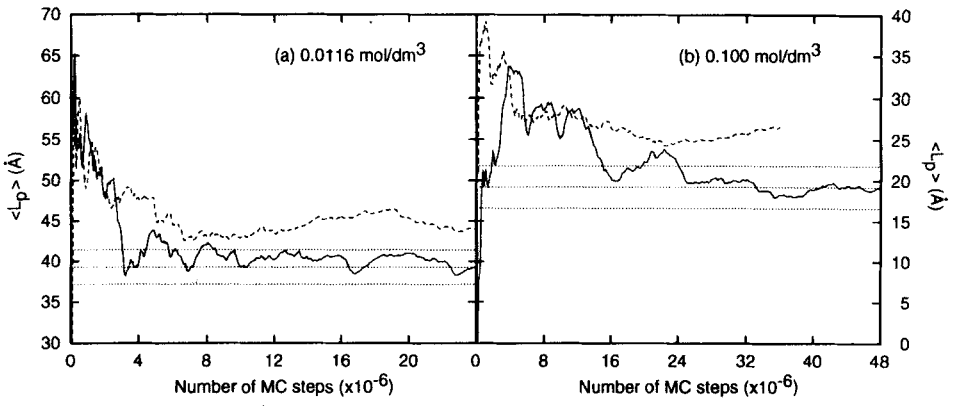

Figure 4 Cumulative average of the polyion persistence length, $\langle L_p \rangle$, as a function of simulation length (number of Monte Carlo steps): (a) 0.0116 mol/dm^3; (b) 0.100 mol/dm^3. —— 'bare' pivots; – – – 'partially clothed' pivots; 'dotted lines show' $\langle L_p \rangle$ over the entire 'bare' pivot simulation $\pm$ 1 standard deviation.

The mean components of the polyion centre-of-mass, $\langle x_{cm} \rangle$, $\langle y_{cm} \rangle$, and $\langle z_{cm} \rangle$, should be identically zero, as the polyion is free to rotate about the origin, and so no directionality in the centre-of-mass components along the cartesian axes should remain after a sufficiently long simulation. On the other hand, this convergence to zero may be expected to be slow. The results displayed in Table 3 show that neither 'bare' pivot simulation at 0.0116 mol/dm^3 or at 0.100 mol/dm^3 was of sufficient length to have all three components of the instantaneous centre-of-mass be zero comfortably within the estimates of error, unlike the results from the corresponding simulations that used 'partially clothed' pivots. Pivotting bath ions along with the chain improves the overall 'tumbling' of the polyion about the origin.

Figures 2–4 are plots of the cumulative averages of $\langle x_{cm} \rangle$, $\langle R_g^2 \rangle$, and $\langle L_p \rangle$ as a function of the simulation length. The convergence seen in simulations that pivot bath ions along with the polyion chain is superior to that of simulations that employed 'bare' polyion chain pivots. The cumulative average tends more quickly towards the final value and displays a lesser tendency to deviate from that value.

As noted earlier, the improvement in the acceptance rate for 'partially clothed' over 'bare' pivots is on the order of only a few percent. However we have shown that the corresponding improvement in the convergence rate for global conformational properties is much greater than that. The reason for this is displayed in Figures 5–7. Figure 5 is a plot of the mean change in the polyion centre-of-mass, $\langle |\Delta \mathbf{R}_{cm}| \rangle$, when a pivot move is accepted, as a function of the length of chain segment pivotted. Figure 1 showed that including some of the surrounding free ions along with the pivotted chain causes pivots of longer chain segments to be accepted more frequently. Additionally, Figure 5 shows that pivots of these long chain segments result, on average, in greater changes in $\mathbf{R}_{cm}$ for 'partially clothed' pivots than for 'bare' pivot moves. What is the overall effect of this? Figure 6 is a plot of the (normalized) distribution of $|\Delta \mathbf{R}_{cm}|$ for both types of pivot moves. Figure 7 is a plot of the ratio of these distributions for 'partially clothed' and 'bare' pivots. Although most pivots, be they 'bare' or 'partially

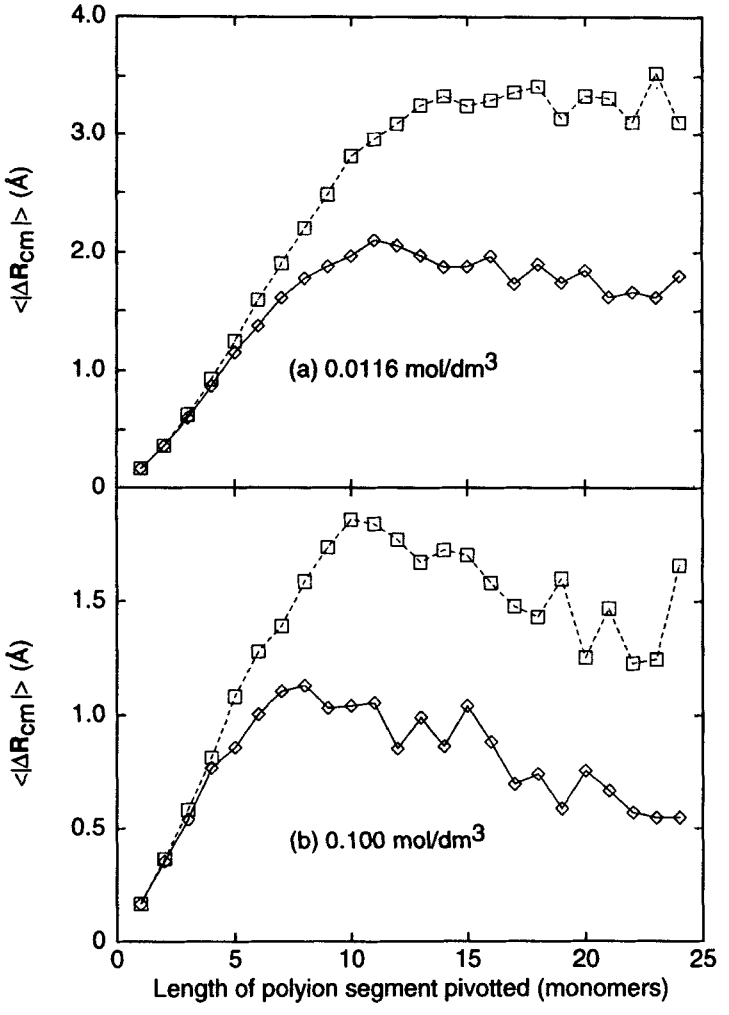

Figure 5 Mean absolute change in the polyion centre-of-mass, $\langle|\Delta \boldsymbol{R}_{cm}|\rangle$, as a function of length of polyion segment pivotted (monomer units) for accepted pivots: (a) 0.0116 mol/dm^3; (b) 0.100 mol/dm^3. —◇— 'bare' pivots; --□-- 'partially clothed' pivots.

clothed', result in small changes in the centre-of-mass (Figure 6), Figure 7 shows that the *proportion* of those pivots that effect large changes (> 5Å) in $\mathbf{R}_{cm}$ is 2 to 10 times greater for 'partially clothed' pivots. In summary, it is not just that longer chain segments are pivotted more frequently when part of the ion atmosphere is pivotted along with the chain, but that *each* such pivot is, on average, considerably more effective in altering the polyion conformation; i.e. larger pivots are being accepted.

Convergence of $\langle L_p \rangle$ is quite slow. In fact, Christos and Carnie [23] were unable to achieve satisfactory estimates of persistence length for their flexible polyion model

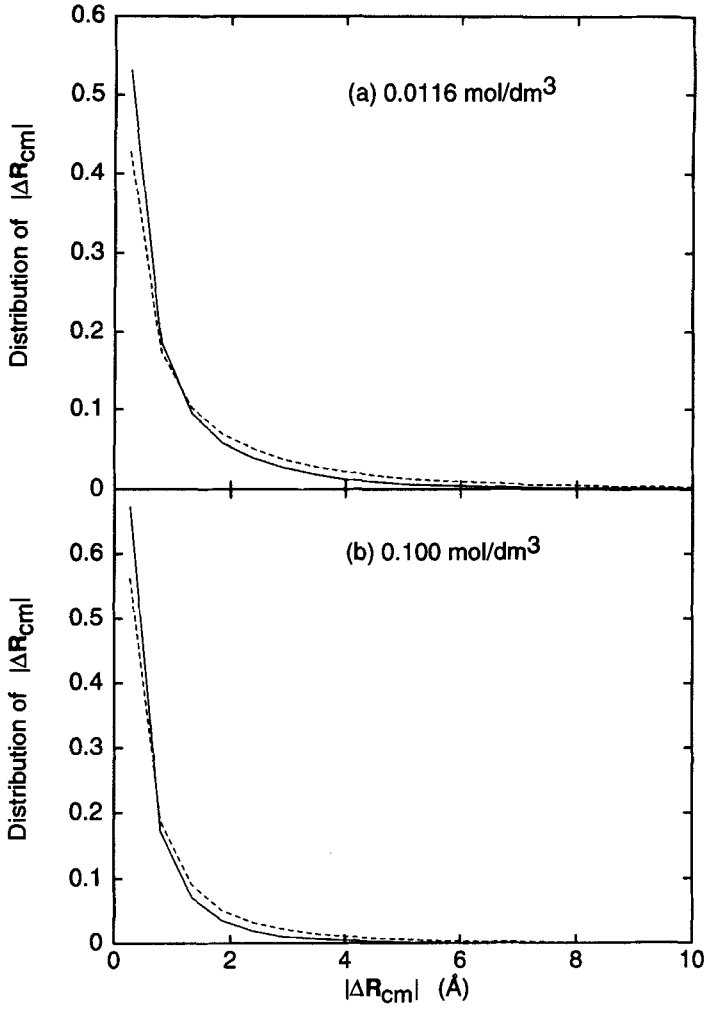

Figure 6 (Normalized) distribution of $|\Delta \mathbf{R}_{cm}|$ for accepted pivots: (a) 0.0116 mol/dm^3; (b) 0.100 mol/dm^3; —— 'bare' pivots; --- 'partially clothed' pivots.

when counterions and co-ions were present. The convergence in $\langle L_p \rangle$ is slow for both 'bare' and 'partially clothed' pivot algorithms and, as mentioned previously, the agreement between these Monte Carlo estimates is not good. In fact, we know that $\langle L_p \rangle$ from the 'bare' pivot simulation at 0.100 mol/dm^3 is not a satisfactory estimate, since it falls below the value found for a shorter polyion ($M = 20$) at the same electrolyte concentration. The accuracy of the estimate of $\langle L_p \rangle$ depends strongly on those of $\langle \cos(\theta) \rangle$ for bonds near the centre of the polyion, and the angles θ for such bonds are altered only when pivots of very large segments of the chain occur. These are naturally the most infrequent events, as we noted. The slow convergence of $\langle L_p \rangle$ is therefore not surprising; the 'partially clothed' pivots should be better in this respect, however.

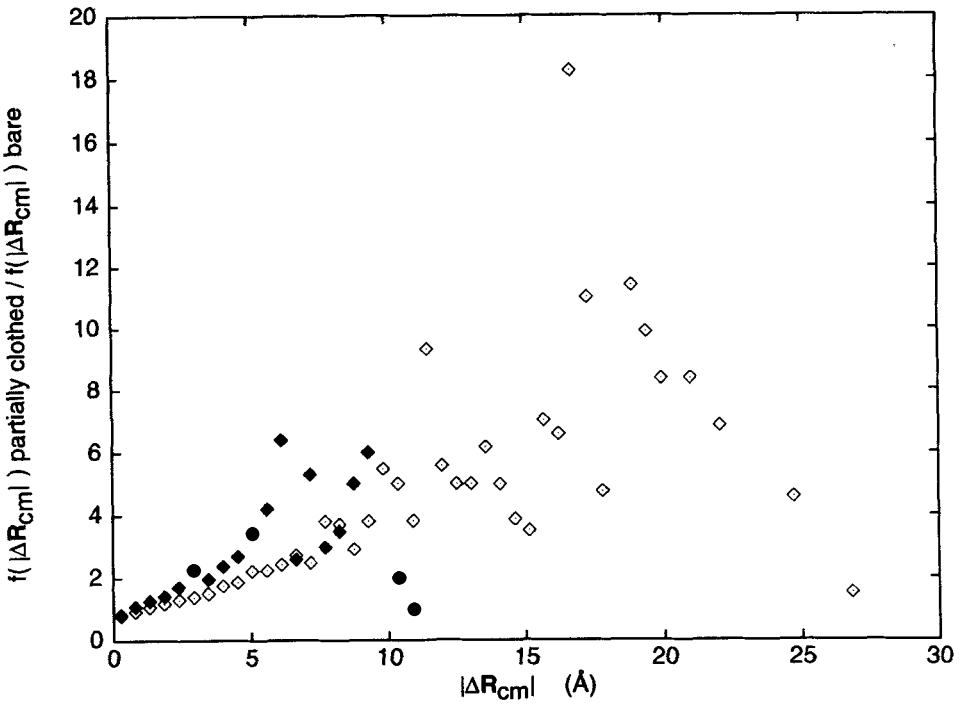

Figure 7 Ratio of distribution of $|\Delta \mathbf{R}_{cm}|$ for 'partially clothed' pivots to that for 'bare' pivots: ◇ 0116 mol/dm^3; ◆ 0.100 mol/dm^3.

One way of examining this is to look at the average $\langle \cos(\theta_i) \rangle$ for the separate "bonds" $i \neq M/2$, shown in Figure 8. These should be symmetric around the central bond, so the discrepancy between the results for $i < M/2$ and $i > M/2$ is some measure of the adequacy of the convergence. The average of the relative differences,

$$\frac{1}{(M/2-1)} \sum_{i=1}^{M/2-1} \frac{|\langle \cos(\theta_i) \rangle - \langle \cos(\theta_{M-i}) \rangle|}{\frac{1}{2}\{\langle \cos(\theta_i) \rangle + \langle \cos(\theta_{M-i}) \rangle\}} \tag{7}$$

is 0.067 for the 'partially clothed' pivot simulation at 0.0116 mol/dm^3, as compared to 0.17 for the 'bare' pivot simulation; the discrepancy is more dramatic at 0.100 mol/dm^3: 0.16 *versus* 0.85. This bears out our expectation that the sampling is far more adequate when some bath ions are pivotted with the polyion segments.

There is thus reason to hope that use of the 'partially clothed' pivots is allowing us to obtain good estimates of the persistence length. The overall convergence rate of other conformational properties are improved by a factor of ~ 2–5. Therefore we consider the extra cpu time required to be clearly justified. In our realization, this amounted to an increase of about 60% in the cpu time required for generation of Markov chain itself (neglecting the comparable additional cpu time necessary to collect conformational properties and ion distributions).

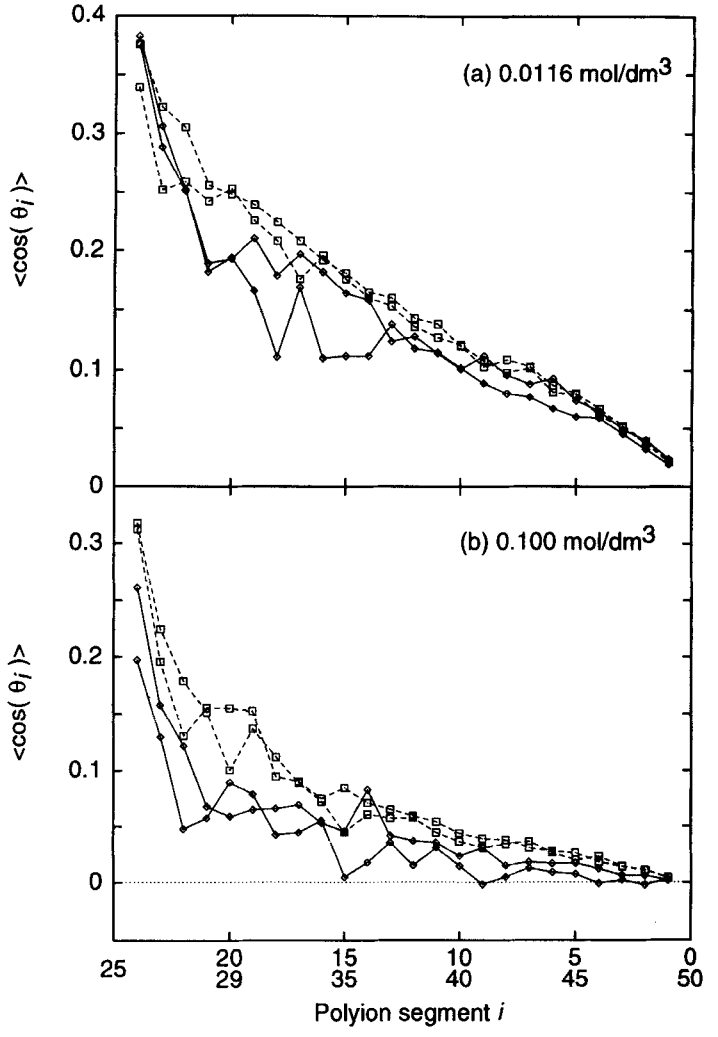

Figure 8 Mean value of $\cos(\theta_i)$ versus i^{th} polyion segment: (a) 0.0116 mol/dm^3; (b) 0.100 mol/dm^3 —◇— 'bare' pivots; --□-- 'partially clothed' pivots. $i = 1$ and 49 are the end segments of the 50 'bead' chain. $\langle\cos(\theta_{i=25})\rangle \equiv 1.0$ and is not shown.

6 DISCUSSION

We have shown that including part of the surrounding ion atmosphere of a polyion chain segment in a pivot move increases the percentage of pivots accepted. This leads to improved convergence rates for the systems described here: a 50 'bead' polyion in either 0.0116 or 0.100 mol/dm^3 supporting electrolyte. However, it may be that an even more salutary combination of P_{pivot} and R_{pivot} exists. Table 4 presents the percentage of pivots accepted, as computed for a series of 200,000-step simulations of the $M = 50$ and

Table 4 Percentage of pivots accepted for various P_{pivot} and R_{pivot} [a]

R_{pivot} [c] (σ units)	P_{pivot} [b]				
	0.0	0.25	0.50	0.75	1.0
1.5	18.2%	19.9%	20.4%	22.4%	19.8%
2.0	18.2%	20.1%	23.0%	24.3%	**22.4%**
2.5	18.2%	**20.5%**	**23.1%**	**24.7%**	21.4%
3.0	18.2%	16.6%	23.0%	24.5%	21.1%

[a] For polyion with $M = 50$ and 0.0116 mol/dm^3 supporting electrolyte. Computed over 200,000 MC steps (of which 40,000 steps are pivot moves), starting from a preequilibrated configuration.

[b] P_{pivot} is the probability that an ion within the volume defined by R_{pivot} will be selected for a forward pivot move. The percent of accepted pivots which is a maximum for each P_{pivot} is in bold.

[c] Bath ions that fall within a radial distance R_{pivot} of any chain ion selected for a trial pivot are each chosen with a probability P_{pivot}.

0.0116 mol/dm^3 system, for various values of P_{pivot} and R_{pivot}. The maximum value is 24.7% for $P_{pivot} = 0.75$ and $R_{pivot} = 2.5\sigma$. Examination of the accepted percentage of pivots as a function of length of chain segment pivotted shows that, as in Figure 1, an increase in the overall pivot acceptance rate is a result of increases in the number of accepted pivots of longer chain segments, and not of end segments only. We also note that, as we anticipated, using $P_{pivot} < 1$ is a better choice than $P_{pivot} = 1$ (i.e. it is a mistake to insist on pivotting all ions within the region defined by R_{pivot}). Note however that when $m_j > m_i$, the factor $(1 - P_{pivot})^{(m_j - m_i)}$ in equation (5) reduces the likelihood that a pivot will be accepted even if $P_{pivot} < 1$. A greater number of ions within the volume defined by R_{pivot} increases the combinatorial possibilities of pivotted/non-pivotted ions that could accompany the chain on its 'reverse' pivot, thus reducing the probability that the same group of ions that accompanied the trial pivot is selected. As a consequence, and as we see from Table 4, the differences among the acceptance rates of pivots for various values of P_{pivot} are not dramatic. Nevertheless, the results of Section 5 indicate that an increase of a few percent in accepted pivots can lead to significant improvements in convergence rates for certain polyion properties. It therefore may be advisable to spend the requisite time exploring various values of P_{pivot} and R_{pivot} in order to find the optimum combination for a particular model.

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References

[1] D. Bratko and V.Vlachy, "Distribution of counterions in the double layer around a cylindrical polyion", *Chem. Phys. Lett.*, **90**, 434 (1982).

[2] M. LeBret and B. H. Zimm, "Monte Carlo determination of the distribution of ions about a cylindrical polyelectrolyte", *Biopolymers*, **23**, 271 (1984).

[3] 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).

[4] M. Rami Reddy, P. J. Rossky and C. S. Murthy, "Counterion spin relaxation in DNA solutions: a stochastic dynamics simulation study", *J. Phys. Chem.*, **91**, 4923 (1987).

[5] P. Mills, C. F. Anderson and M. T. Record, Jr., "Monte Carlo studies of counterion-DNA interactions. Comparisons of the radial distribution of counterions with predictions of other polyelectrolyte theories", *J. Phys. Chem.*, **89**, 3984 (1985).

[6] P. Mills, C. F. Anderson and M. T. Record, Jr., "Grand canonical Monte Carlo calculations of thermodynamic coefficients for a primitive model of DNA-salt solution", *J. Phys. Chem.*, **90**, 6541 (1986).

[7] M. D. Paulsen, B. Richey, C. F. Anderson and M. T. Record, Jr. "The salt dependence of the preferential interaction coefficient in DNA solutions as determined by grand canonical Monte Carlo simulations", *Chem. Phys. Lett.*, **139**, 448 (1987); "Erratum", *Chem. Phys. Lett.*, **143**, 115 (1988).

[8] V. Vlachy and A. D. J. Haymet, "A grand canonical simulation study of polyelectrolyte solutions", *J. Chem. Phys.*, **84**, 5874 (1986).

[9] L. G.Nilsson, L. Nordenskiöld and P. Stilbs, "Macroscopic counterion diffusion in solutions of cylindrical polyelectrolytes. 2. Ion correlation effects", *J. Phys. Chem.*, **91**, 6210 (1987).

[10] L. Guldbrand and L. Nordenskiöld, "Brownian dynamics simulation of counterion dynamics in cylindrical polyelectrolyte solutions", *J. Phys. Chem.*, **91**, 5714 (1987).

[11] H. L. Gordon and S. Goldman, "Simulations of the counterion and solvent distribution functions around two simple models of a polyelectrolyte", *J. Phys. Chem.*, **96**, 1921 (1992).

[12] G. Weill, "Polyelectrolytes-counterion interactions", in *Macromolecules*, H. Benoit and P. Rempp, eds., Pergamon Press, Oxford (1982).

[13] R. Bacquet and P. J. Rossky, "Ionic atmosphere of rodlike polyelectrolytes. A hypernetted chain study", *J. Phys. Chem.*, **88**, 2660 (1984).

[14] E. Gonzales-Tovar, M. Lozada-Cassou and D. Henderson, "Hypernetted chain approximation for the distribution of ions around a cylindrical electrode. II. Numerical solution for a model cylindrical polyelectrolyte", *J. Chem. Phys.*, **83**, 361 (1985).

[15] T. G. Wensel, C. F. Meares, V. Vlachy and J. B. Matthew, "Distribution of ions around DNA, probed by energy transfer", *Proc. Natl. Acad. Sci. USA*, **83**, 3267 (1986).

[16] R. M. Fuoss, A. Katchalsky and S. Lifson, "The potential of an infinite rod-like molecule and the distribution of the counter ions", *Proc. Natl. Acad. Sci. USA*, **37**, 579 (1951).

[17] T. Alfrey, Jr., P. W. Berg and H. Morawetz, "The counterion distribution in solutions of rod-shaped polyelectrolyes", *J. Polymer Sci.*, **7**, 543 (1951).

[18] A. Baumgaïtner, "Unscreened polyelectrolyte chain in *d* dimensions: A Monte Carlo simulation", *J. Physique Lett.*, **45**, L515 (1984).

[19] J. M. Victor and J. P. Hansen, "On the form factor of two-dimensional polyelectrolytes under strong screening conditions", *Europhys. Lett.*, **3**, 1161 (1987).

[20] J. P. Valleau, "Flexible polyelectrolyte in ionic solution: A Monte Carlo study", *Chem. Phys.*, **129**, 163 (1989).

[21] S. L. Carnie, G. A. Christos and T. P. Creamer, "Monte Carlo simulations of polyelectrolytes: Isolated fully ionized chains with screened Coulomb interactions", *J. Chem. Phys.*, *89*, 6484 (1988).

[22] G. A. Christos and S. L. Carnie, "Monte Carlo simulations of partially ionized polyelectrolytes: Shape and distribution functions", *J. Chem. Phys.*, **91**, 439 (1989).

[23] G. A. Christos and S. L. Carnie, "Computer simulations of polyelectrolyte chains in salt solution", *J. Chem. Phys.*, **92**, 7661 (1990).

[24] G. A. Christos, S. L. Carnie and T. P. Creamer, "Monte Carlo simulations of partially ionized polyelectrolytes: Conformational properties", *Macromolecules*, **25**, 1121 (1992).

[25] C. E. Woodward and B. Jönsson, "Monte Carlo and mean field studies of a polyelectrolyte in salt solution", *Chem. Phys.*, **155**, 207 (1991).

[26] M. Granfeldt, B. Jönsson and C. E. Woodward, "A mean-field Monte Carlo technique for studies of electric double layers and flexible polyelectrolytes", *J. Phys. Chem.*, **96**, 10080 (1992).

[27] C. Brender, M. Lax and S. Windwer, "Monte Carlo study of polyelectrolyte behavior. I. Technique", *J. Chem. Phys.*, **74**, 2576 (1981).

[28] C. Brender, M. Lax and S. Windwer, "Monte Carlo study of polyelectrolyte behaviour. II. Configurational properties", *J. Chem. Phys.*, **80**, 886 (1984).
[29] C. Brender, "Coil to rod transitions in Monte Carlo simulations of a short polyelectrolyte. I. New thermal and screening effects", *J. Chem. Phys.*, **92**, 4468 (1990).
[30] C. Brender, "Coil to rod transitions in Monte Carlo simulations of a short polyelectrolyte. II. Natural screening and a new thermal effect", *J. Chem. Phys.*, **93**, 2736 (1990).
[31] C. Brender, "Coil to rod transitions in Monte Carlo simulations of a short polyelectrolyte. III. Contact as a new type of bond", *J. Chem. Phys.*, **94**, 3213 (1990).
[32] C. Brender and M. Danino, "The average number of kinks of a short polyelectrolyte chain: A Monte Carlo Study", *J. Chem. Phys.*, **97**, 2119, 1992.
[33] C. Brender, "The mean straight length of a short polyelectrolyte: A Monte Carlo study", *J. Phys. Chem.*, **96**, 5553 (1992).
[34] C. Brender and M. Danino, "Internal distances in short polyelectrolytes: A Monte Carlo study", *Phys. Rev. E*, **48**, 3717 (1993).
[35] H. H. Hooper, H. W. Blanch and J. M. Prausnitz, "Configurational properties of partially ionized polyelectrolytes from Monte Carlo simulation", *Macromolecules*, **23**, 4820 (1990).
[36] H. H. Hooper, S. Beltran, A. P. Sassi, H W. Blanch and J. M. Prausnitz, "Monte Carlo simulations of hydrophobic polyelectrolytes. Evidence for a structural transition in response to increasing chain ionization", *J. Chem. Phys.*, **93**, 2715 (1990).
[37] A. P. Sassi, S. Beltran, H. H. Hooper, H W. Blanch, J. Prausnitz and R. A. Siegel, "Monte Carlo simulations of hydrophobic weak polyelectrolytes: Titration properties and pH-induced structural transitions for polymers containing weak electrolytes", *J. Chem. Phys.*, **97**, 8767 (1992).
[38] C. Reed and W. Reed, "Monte Carlo test of electrostatic persistence length for short polymers", *J. Chem. Phys.*, **92**, 6916 (1990).
[39] C. E. Reed and W. F. Reed, "Monte Carlo electrostatic persistence lengths compared with experiment and theory", *J. Chem. Phys.* **94**, 8479 (1991).
[40] C. E. Reed and W. F. Reed, "Monte Carlo study of titration of linear polyelectrolytes", *J. Chem. Phys.*, **96**, 1609 (1992).
[41] C. E. Reed and W. F. Reed, "Monte Carlo study of light scattering by linear polyelectrolytes", *J. Chem. Phys.*, **97**, 7766 (1992).
[42] P. G. Higgs and H. Orland, "Scaling behaviour of polyelectrolytes and polyampholytes: Simulation by an ensemble growth method", *J. Chem. Phys.*, **95**, 4506 (1991).
[43] M. Severin, "Thermal maximum in the size of short polyelectrolyte chains. A Monte Carlo study", *J. Chem. Phys.*, **99**, 628 (1993).
[44] A. Robinson de Souza and L. Degrève, "Computer simulation of configurational properties of partially ionized polyelectrolytes", *J. Molec. Struct. (Theochem)*, **282**, 167 (1993).
[45] Th. M. A. O. M. Barenbrug, J .A. M. Smit and D. Bedeaux, "Influence of charge mobility on the equilibrium properties of polyelectrolytes in salt solutions: A Monte Carlo study", *Macromolecules*, **26**, 6864 (1993).
[46] C. Seidel, H. Schlacken and I. Müller, "Conformational properties of weakly charged polyelectrolytes from Monte Carlo simulations", *Macromol. Theory Simul.*, **3**, 333 (1994).
[47] M. Lal, 'Monte carlo' Computer simulation of chain molecules. I.", *Mol. Phys.*, **17**, 57 (1969).
[48] B. MacDonald, N. Jan, D. L. Hunter and M. O. Steinitz, "Polymer conformations through 'wiggling'", *J. Phys. A*, **18**, 2627 (1985).
[49] N. Madras and A. D. Sokol, "The pivot algorithm: A highly efficient Monte Carlo method for the self-avoiding walk", *J. Stat. Phys.*, **50**, 109 (1988).
[50] J. P. Valleau and S. G. Whittington, "A Guide to Monte Carlo for Statistical Mechanics: Highways", *in Statistical Mechanics, Part A: Equilibrium Techniques*, B. J. Berne, ed., Plenum Press, New York (1979).
[51] O. F. Olaj and K. H. Pelinka, "Pair distribution and pair potential of lattice model chains under theta conditions, 1", *Makromol. Chem.*, **177**, 3413 (1976).
[52] D. L. Hunter, N. Jan and B. MacDonald, "On the correction-to-scaling exponent of linear polymers in two dimensions", *J. Phys. A*, **19**, L543 (1986).
[53] J. J. Freire and A. Horta, "Mean reciprocal distances of short polymethylene chains. Calculation of the translational diffusion coefficient of n-alkanes", *J. Chem. Phys.*, **65**, 4049 (1976).
[54] G. Zifferer, "Monte Carlo simulation of tetrahedral chains. 1. Very long (athermal) chains by pivot algorithm", *Macromolecules*, **23**, 3166 (1990).
[55] G. Zifferer, "Monte Carlo simulation of tetrahedral chains, 3. Star-shaped polymers by pivot algorithm", *Makromol. Chem.*, **191**, 2717 (1990).
[56] S. D. Stellman and P. J. Gans, "Efficient computer simulation of polymer conformation. I. Geometric properties of the hard-sphere model", *Macromolecules*, **5**, 516 (1972).

[57] S. D. Stellman and P. J. Gans, "Computer simulation of polymer conformation. II. Distribution function for polymers with excluded volume", *Macromolecules*, **5**, 720 (1972).
[58] J. C. Owicki and H. A. Scheraga, "Preferential sampling near solutes in Monte Carlo calculations on dilute solutions", *Chem. Phys. Lett.*, **47**. 600 (1977).
[59] R. Friedberg and J. E. Cameron, "Test of the Monte Carlo method: Fast simulation of a small Ising lattice", *J. Chem. Phys.*, **52**, 6049 (1970).
[60] J. J. Morales and M. J. Nuevo, "Statistical error methods in computer simulations", *J. Comput. Phys.*, **89**, 432 (1990).