

A Novel Simulation Architecture of Configurational-Bias Gibbs Ensemble Monte Carlo for the Conformation of Polyelectrolytes Partitioned in Confined Spaces

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Received Mar. 31, 2003; Revised Sept. 18, 2003

Abstract: By applying a configurational-bias Gibbs ensemble Monte Carlo algorithm, priority simulation results regarding the conformation of non-dilute polyelectrolytes in solvents are obtained. Solutions of freely-jointed chains are considered, and a new method termed strandwise configurational-bias sampling is developed so as to effectively overcome a difficulty on the transfer of polymer chains. The structure factors of polyelectrolytes in the bulk as well as in the confined space are estimated with variations of the polymer charge density.

Keywords: polyelectrolyte, configurational-bias, Gibbs ensemble Monte Carlo, chain conformation, structure factor, Debye-Hückel interaction.

Introduction

Polyelectrolytes, one of the typical complex fluids, are polymers bearing ionizable groups. They dissolve in water due to the electrostatic repulsion between charged monomers,¹ even though water is a poor solvent for most of synthetic polymers. The conformational properties of polyelectrolytes are strongly affected by geometric confinement.²⁻⁴ The problem of confined polyelectrolytes is relevant to numerous applications such as in size-exclusion chromatography, vascularized spaces, and thin-film processing. Research trend has become increasingly important in the design of either micro-biochips or microfluidic devices and the preparation of nanocomposites.

Even if the polyelectrolytes exist in an unbounded free space, the explicit understanding of conformation is not easy. The polyelectrolytes in confined spaces result in more difficult problem. The difficulty of performing experiments makes rigorous simulations the more important. From the modeling the concentration partitioning of colloid particles between the bulk and the slit-like pore, Chun and Phillips⁵ recognized the usefulness of Gibbs ensemble Monte Carlo (GEMC) simulations to study the static properties in confined spaces. It is obvious that the canonical ensemble MC

is not available to simulate each of the coexisting subsystems. Recently, Park *et al.*³ examined the single chain problem with the effects of the intramolecular interactions using a mean field approximation, where the interchain interaction was safely neglected.

In contrast to the small molecules, when the GEMC is applied to the polymer chains, the transfer of large molecules between subsystems is rarely accepted always due to the overlapping of the molecules. By employing the configurational-bias (CB) sampling, however, one can get efficacy in sampling the trial conformations of polyelectrolytes. The CB technique enhances significantly the acceptance rate compared to the naive method that samples the whole chain conformation at each trial transfer step.^{4,6}

Since the CBGEMC with sampling all monomers is the time-consuming simulation, therefore, the strandwise CBGEMC is newly developed. Here, a strand is defined by dividing a polyelectrolyte chain into several domains in its sequence. The ultimate examination of the present simulation aims the estimation of partition coefficient, however, this communication addresses the results devoting the effect of electrostatic interactions on the conformation of polyelectrolytes in both the bulk and the confined space. A charged cylindrical pore is considered for the confined space, where the size of the pore is comparable to or larger than the radius of gyration of the polymer.

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Strandwise Configurational-Bias Gibbs Ensemble Monte Carlo Method

GEMC Simulation without Volume Exchanges. The GEMC method has been successfully applied to the studies of phase equilibria ranging from Lennard-Jones fluids to molecular solutions. In the original GEMC scheme, volumes are exchanged between subsystems to find the equilibrium state, along with the canonical NVT moves of the particles within each subsystem. However, the volume exchange process (i.e., NPT) is not necessary if the relevant system is guaranteed to be homogeneous and stable at any concentration,⁵ likewise this study.

For the CBGEMC, each simulation boxes are constructed as shown in Figure 1. The total probability distribution of subsystems is

$$P(N) = P_b(N_b)P_{cs}(N_{cs}) \quad (1)$$

where $N (= N_b + N_{cs})$ is the total number of polyelectrolyte chains, and N_b and N_{cs} are the numbers of chains existing in the bulk and the confined space, respectively. For N_b chains in the bulk of volume V_b , the probability distribution is given by

$$P_b(N_b) = \frac{V_b^{N_b}}{N_b!} \exp\left[-\frac{1}{k_B T} \sum_{i < j} E(\mathbf{r}_i, \mathbf{r}_j)\right] \prod_{(i,j)} \delta(|\mathbf{r}_i - \mathbf{r}_j| - 2a) \quad (2)$$

where $k_B T$ is the Boltzmann thermal energy, \mathbf{r}_i the position vector of i -th monomer bead, and a the radius of bead. The long-range energy of Coulomb interaction $E(\mathbf{r}_i, \mathbf{r}_j)$ between a pair of monomers is given by⁷

$$E(\mathbf{r}_i, \mathbf{r}_j) = \begin{cases} \infty, & \text{if } |\mathbf{r}_i - \mathbf{r}_j| < 2a \\ Q_i Q_j \frac{\exp(-\kappa|\mathbf{r}_i - \mathbf{r}_j|)}{|\mathbf{r}_i - \mathbf{r}_j|}, & \text{otherwise} \end{cases} \quad (3)$$

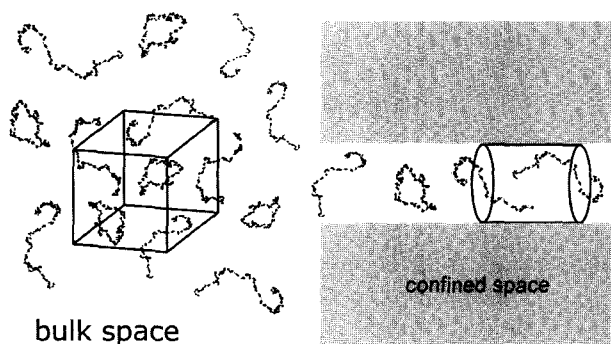


Figure 1. A schematic of polyelectrolytes in the bulk as well as in the confined space of narrow pore, where the periodic boxes are illustrated.

where Q_i corresponds to the charge of i -th monomer. The product of Dirac delta functions in Eq. 2 represents the constraint of the freely-jointed bead-chain with neighboring segments separated by twice the bead radius.³ Similarly, the probability distribution for N_{cs} chains in the pore of volume V_{cs} is

$$P_{cs}(N_{cs}) = \frac{V_{cs}^{N_{cs}}}{N_{cs}!} \exp\left[-\frac{1}{k_B T} \sum_{i < j} E(\mathbf{r}_i, \mathbf{r}_j) - \frac{1}{k_B T} \sum_i Q_i \phi(\mathbf{r}_i)\right] \prod_{(i,j)} \delta(|\mathbf{r}_i - \mathbf{r}_j| - 2a) \quad (4)$$

where $\phi(\mathbf{r})$ is the electrostatic potential at the position \mathbf{r} due to the charged wall. This study employs the Coulomb interactions treated at the Debye-Hückel (or Yukawa) approximation level.

Charged beads are located at both ends of the chain and evenly distributed at every fixed number of monomers. For the NVT moves, a monomer is chosen with equal probability and a random trial is generated under a constraint of the freely-jointed chain. The acceptance criteria for the move in the specified subsystem is given by

$$Rand < \min\left[1, \exp\left(-\frac{\Delta E}{k_B T}\right)\right] \quad (5)$$

where $Rand$ is a uniform random number. The random exchange of grand canonical μ VT ensemble is then performed for the condition of chemical potential equilibrium. The transfer is accepted if

$$Rand < \min\left[1, \frac{N_d V_r}{(N_r + 1) V_d} \exp\left(-\frac{(\Delta E_d + \Delta E_r)}{k_B T}\right)\right] \quad (6)$$

where the subscripts d and r indicate the donating and receiving subsystems, respectively.

Strandwise Configurational-Bias Sampling. The isolated polymer chain can be modeled by a self-avoiding walk of M monomers.^{1,2} The chain is divided into a number of pieces with a strand as shown in Figure 2. The number of monomers in a strand may be varying depending upon the charge distribution of the chain and the monomer concentration of the

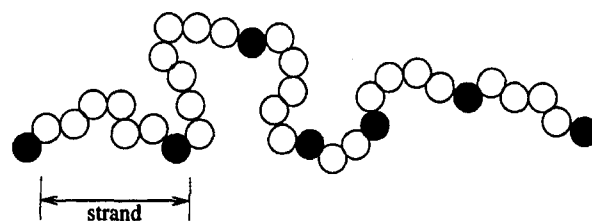


Figure 2. Schematic drawing of the polyelectrolyte chain divided into strands. Dark beads denote the charged monomers.

subsystem. For a neutral polymer that has only the excluded volume interaction, the optimal strand length may be approximately given as the ν -th power of an average size of the voids in the solution. For charged polymers, the charged monomers have strong preferences in their positions to lower the potential energy. An optimal strand size may be determined in such a way that each strand has a charged monomer at the end of each strand.

Let us describe a brief algorithm for the strandwise CB sampling for transfer of a chain from the bulk to the pore as an example. The first segment is assigned as a strand since it is always charged in the present model. We find N_{1st} different positions randomly for the insertion of the first monomer into the pore, and then calculate the correct Boltzmann weight $w_1(j) = \exp[-E(j)/k_B T]$, where $E(j)$ is the interaction energy of the first monomer at r_j ($j = 1, 2, \dots, N_{1st}$). According to the probability distribution $\text{Pr}(j) = w_1(j)/\sum_j w_1(j)$, we select one among N_{1st} trial positions, and N_{str} strands are generated with an appropriate length starting from the end position of the previous strand. Both the calculation of $w_2(j) = \exp[-E(j)/k_B T]$ for j -th strand with $j = 1, 2, \dots, N_{str}$ and selecting one among N_{str} trial strands based on the probability distribution are repeating until the end of the selected chain. We calculate the Rosenbluth factor of the new conformation,^{6,8}

$$W(n) = \prod_i \left[\sum_j w_i(j) \right]. \quad (7)$$

The next stage calculates the Rosenbluth factor of the old conformation in the bulk, by generating $N_{1st}-1$ trial positions for the first monomer and $N_{str}-1$ trial strands for each strand,

$$W(o) = \prod_i \left[\sum_j \tilde{w}_i(j) \right]. \quad (8)$$

The trial transfer is either accepted or rejected in accordance with probability criterion,

$$A(o \rightarrow n) = \min \left[1, \frac{N_b V_{cs} W(n)}{(N_{cs} + 1) V_b W(o)} \right]. \quad (9)$$

An analogous algorithm is used for the transfer from the pore to the bulk. An appropriate strand length is determined dynamically, depending upon the concentration of the object subsystem as well as upon the polyelectrolyte charge density.

Condition of Super Detailed Balance. This condition relevant to the chain transfer step can be expressed as

$$P(o)T(o \rightarrow n)A(o \rightarrow n) = P(n)T(n \rightarrow o)A(n \rightarrow o). \quad (10)$$

Here, $T(o \rightarrow n) = \exp[-E(n)/k_B T]/W(n)$ and $T(n \rightarrow o) = \exp[-E(o)/k_B T]/W(o)$ indicate transition probabilities with dummy notations of o and n standing for old and new configurations. From the super detailed balance, one can derive a condition for the acceptance probability,

$$\frac{A(o \rightarrow n)}{A(n \rightarrow o)} = \frac{N_b V_{cs} W(n)}{(N_{cs} + 1) V_b W(o)}. \quad (11)$$

Eq. 9 satisfies Eq. 11, owing to the consequence of the acceptance criteria.

Simulation Results

A hypothetical cubic box made with Cartesian coordinates is applied to the bulk, and the periodic boundary conditions are imposed for all directions. For the confined space, the periodic boundary conditions are embedded along the axial direction of a cylindrical box. The wall of the space has uniform surface charge density σ_w , and the freely-jointed chain has contour length $L = l(M - 1)$, where $l = 2a$ is the segmental length. All the variables are nondimensionalized by the segmental length and the characteristic time at constant $k_B T$. Charged beads are placed with equal spacing of inverse polyelectrolyte charge density $1/\sigma_p$ along the chain contour. Simulations are performed with variations of both N and L . About 1×10^5 updates of the position of each monomer are performed, and then chain transfer is attempted at 10 to 100 updates per monomer. Suitable adjusting this value is necessary to guarantee the relaxed subsystem. Equilibrium state can be determined by monitoring the change of total energy as a simulation proceeds, in which the simulation period is divided into 50 blocks of configurations. The numerical code was self-made in C++.

Chain Conformations. Snapshots of each simulation boxes are displayed in Figure 3. The moderate polyelectrolyte charge density σ_p of 0.1 is considered, which means the charged monomers are located at every 10 beads. As the elementary length units, l is given 1.0. Debye screening length κ^{-1} (i.e., in dimensional, $1/\sqrt{e^2 \sum_i z_i^2 n_i / \epsilon k_B T}$) is provided as 5.0, and Bjerrum length λ_B (i.e., in dimensional, $e^2 / 4\pi \epsilon k_B T$) is given 2.0. Here, e represents the elementary charge, Z_i the amount of charge on monomer i , n_i the ionic concentration, and ϵ the dielectric constant.

Although the other snapshots are not given, results show that the chains have rod-like conformations in the dilute concentration regime caused by the repulsion among the charged monomers. In the moderate concentration regime the intrachain electrostatic repulsions are screened and the chains are indeed overlapped. The dilute polyelectrolyte chains reside near the center of confined space and stretch along the axial direction once the polymer-wall interaction is repulsive. When the chain concentration becomes moderate however, such trends are generally disappeared. The estimation of radius of gyration R_G provided in Table I supports this behavior. In the bulk, one takes $\langle R_G^2 \rangle = \langle \sum_{i,j} (\mathbf{r}_i - \mathbf{r}_j)^2 \rangle / N$ and $\langle R_G^2 \rangle = \langle R_{G,\parallel}^2 \rangle + \langle R_{G,\perp}^2 \rangle$ is introduced in the pore identifying the anisotropy. The radius of gyration is decreased with increasing the chain concentration, where its value in the pore is higher than that in the bulk.

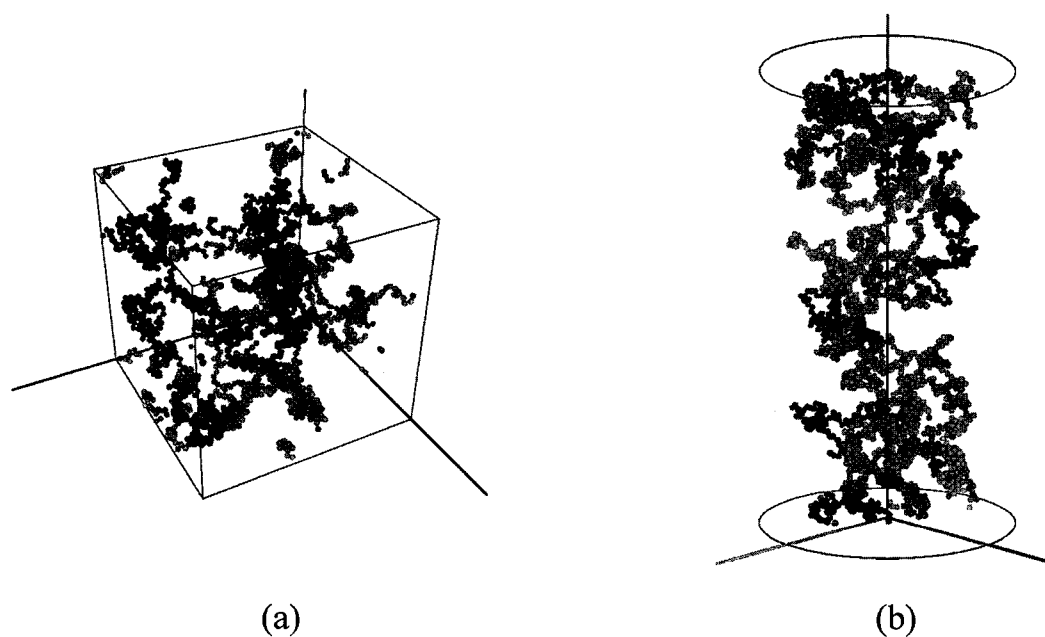


Figure 3. Snapshots of polyelectrolytes (a) in the bulk and (b) in the confined space of charged pore by performing the CBGEMC simulation with total configurations of 3×10^6 . Total 60 chains are introduced, and each chain consists of 100 monomers.

Structure Factor. The structure factor represents the microstructural information that gives all length scale data. The scattering wave vector \mathbf{q} has a magnitude $|\mathbf{q}| = 2|k| \sin(\theta/2) = (4\pi/\lambda) \sin(\theta/2)$, where k is the wave vector, λ the wavelength in the dispersion medium, and θ the scattering angle.⁷ In the bulk, we can define the spherically-averaged static structure factor $S_s(\mathbf{q})$ for all monomers of all chains, which is the Fourier transform of the pair correlation function $g(\mathbf{r}) = \langle \sum_{m,n} \delta(\mathbf{r} - \mathbf{r}_m) \delta(\mathbf{r} - \mathbf{r}_n) \rangle$. One obtains

$$S_s(\mathbf{q}) \equiv \left\langle \frac{1}{NM} \left| \sum_{i < j}^{N,M} \exp(-i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)) \right|^2 \right\rangle \quad (12)$$

$$= \frac{1}{NM} \int d\mathbf{r} \exp(i\mathbf{q} \cdot \mathbf{r}) g(\mathbf{r}) .$$

In the pore, the static structure factor parallel to the wall is

Table I. Estimations of Radius of Gyration in Each Sub-system for Different Polymer Charge Density, σ_p , with $M = 100$ and $\sigma_w = 0.1$

σ_p	$\langle R_G^2 \rangle_{bulk}$		$\langle R_G^2 \rangle_{pore}$	
	$N = 20$	$N = 60$	$N = 20$	$N = 60$
0.0	21.1	6.7	30.6	8.1
0.05	22.6	6.3	32.9	9.6
0.10	36.6	10.1	41.4	12.5
0.20	61.0	21.8	64.4	24.0

evaluated via $S_{s,t}(\mathbf{q}) = S_{s,z}(q_z)$.

As shown in Figures 4 and 5, the structure factor is constant at lower value of q and then provides a decreasing tendency with increasing the q value. The $S_s(q)$ is an oscillatory function at intermediate values of q , but its σ_p dependency is relatively decreased for larger value of q . The slope between q and $S_s(q)$ is higher in the bulk compared to that in the

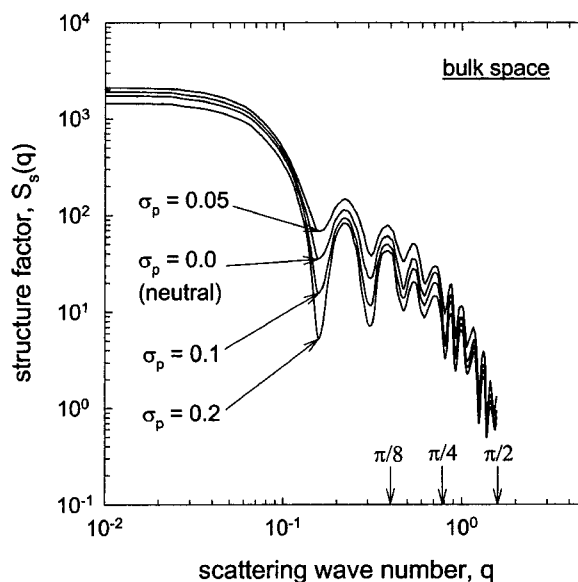


Figure 4. Static structure factor, $S_s(q)$, in the bulk for various polyelectrolyte charge density, σ_p , at $N = 20$, $L = 160$, $\kappa = 0.2$, $\lambda_B = 2.0$, and $\sigma_w = 0.1$.

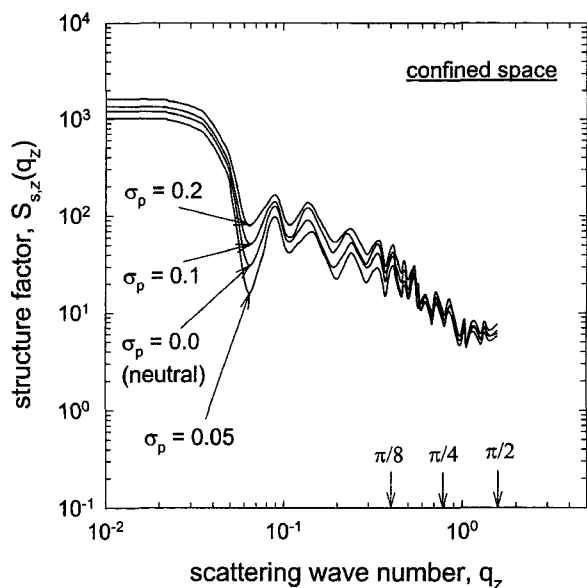


Figure 5. Static structure factor, $S_{s,z}(q_z)$, in the confined space for various polyelectrolyte charge density, σ_p , at $N = 20$, $L = 160$, $\kappa = 0.2$, $\lambda_B = 2.0$, and $\sigma_w = 0.1$.

pore. This means polyelectrolyte chains in the bulk experience the collapsed globular conformation having strong correlations, whereas they become elongated with the self-avoiding walks conformation in the pore. As the σ_p increases, the structure factor in the bulk is decreased for a given value of q . In the confined space, however, the opposite behavior is observed due to the confining wall effect.

Conclusions

Conventional MC simulations are restricted to examining the conformation of non-dilute polyelectrolytes partitioned in confined spaces, for which a novel MC architecture with strandwise CB Gibbs ensemble has successfully been developed. This communication presented the distinct results of structure factor with variations of the polyelectrolyte charge density. In the future study, extensive results will be addressed by encouraging the present codes.

Acknowledgements. This work was supported by the Basic Research Fund (KOSEF: R01-2001-000-00411-0). The author also acknowledges helpful comments on the MC study of non-dilute polyelectrolytes provided by the Theory Group of Max-Planck Institut für Polymerforschung at Mainz during the visiting research funded by the DFG.

References

- (1) K. Kremer and K. Binder, *Comput. Phys. Rep.*, **7**, 259 (1988)
- (2) I. Teraoka, *Prog. Polym. Sci.*, **21**, 89 (1996).
- (3) P. J. Park, M. -S. Chun, and J. -J. Kim, *Macromolecules*, **33**, 8850 (2000).
- (4) G. F. Hermesen, B. A. de Geeter, N. F. A. van der Vegt, and M. Wessling, *Macromolecules*, **35**, 5267 (2002).
- (5) M. -S. Chun and R. J. Phillips, *AIChE J.*, **43**, 1194 (1997).
- (6) D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithm to Applications*, 2nd Ed., Academic Press, New York, 2002.
- (7) M. -S. Chun and H. S. Lee, *Macromole. Res.*, **10**, 297 (2002)
- (8) M. N. Rosenbluth and A. W. Rosenbluth, *J. Chem. Phys.*, **23**, 356 (1955).