Macromolecular Research, Vol. 10, No. 6, pp 297-303 (2002)

Macromolecular Research

Volume 10, Number 6 December 31, 2002

Investigations on the Chain Conformation of Weakly Charged Polyelectrolyte in Solvents by Using Efficient Hybrid Molecular Simulations

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Received Aug. 8, 2002; Revised Dec. 2, 2002

Abstract: We have investigated the microstructural properties of a weakly charged polyelectrolyte modeled with both Hookean spring and Debye-Hückel potential, by employing a novel hybrid scheme of molecular dynamics (MD) and Monte Carlo (MC) simulations. Although the off-lattice pivot step facilitates the earlier computations stage, it gives rise to oscillations and hinders the stable equilibrium state. In order to overcome this problem, we adopt the MC off-lattice pivot step in early stage only, and then switch the computation to a pure MD step. The result shows that the computational speed-up compared to the previous method is entirely above 10 to 50, without loss of the accuracy. We examined the conformations of polyelectrolyte in solvents in terms of the end-to-end distance, radius of gyration, and structure factor with variations of the screening effects of solvent and the monomer charges. The emphasis can favorably be given on the elongation behavior of a polyelectrolyte chain, with observing the simultaneous snapshots.

Keywords: polyelectrolyte, molecular dynamics, Monte Carlo simulation, chain conformation, structure factor.

Introduction

Polyelectrolytes, one of the typical complex fluids, are polymers bearing ionizable groups which can dissociate into charged polymer chains in polar solvents. Due to their fascinating conformational changes in solvents, polyelectrolytes have always stimulated interests from a fundamental as well as from a technological point of view. One of the main technologically important properties of polyelectrolytes is that they dissolve in water due to the electrostatic repulsion between charged monomers,[1-3] even though water is a poor solvent for most of synthetic polymers. Especially, the behavior of polyelectrolytes in confined spaces is connected with numerous applications including separations with gel electrophoresis, size-exclusion chromatography, and porous membrane as well as transports within vascularized spaces, renal glomerular channel, and other biological media.[4,5] Very

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1598-5032/12/297-07

recently, an understanding of polyelectrolytes has become increasingly important in the design of microchannels for micro-biochips and micro/nanofluidic devices.

However, the theoretical understanding of polyelectrolytes is less developed than that of the properties of neutral polymers. In addition to the occurrence of long-range interactions, the large number of degrees of freedom of the counter-ions and their fluctuations form more difficult problem. A comparison between experiment and theory is often very difficult because of different regions of validity concerning the density of the solution. Scattering experiments need a certain contrast and therefore it is almost impossible to study extremely dilute solutions, which are the topic of most theories. In such a situation, computer simulations have the important possibility to build a bridge between theory and experiment as they can test theoretical aspects as well as experimentally measurable quantities under well controllable conditions.[6,7]

There exist a good number of papers on the properties of polyelectrolyte in solvents. In late 1990s, Dobrynin *et al.*[2] developed a scaling theory that describes how, with varying solvent quality or charge on the chain, the polyelectrolyte in poor solvents undergoes a cascade of abrupt transitions between pearl-necklace configurations with different numbers of beads.[8] They addressed that the length of the necklace globule is proportional to the total polymer charge by using Monte Carlo (MC) simulations. Micka and Kremer[7] examined the polyelectrolyte conformation by exploiting hybrid of Molecular Dynamics (MD) and MC algorithm. In their study, polyelectrolytes were described with both the Hookean model and the Debye-Hückel (D-H) potential so as to include the screening effect resulting from salts as well as counter-ions. They predicted the persistence length and important conformational properties (e.g., radius of gyration, end-to-end distance, and structure factor) for various chain lengths, Debye lengths, and so on.[9,10] Recently, the hybrid algorithm was utilized for more complicated problems reported by Lyulin *et al.*.[11] Besides the D-H potential, the finitely extendable nonlinear elastic (FENE) potential and generalized Lennard-Jones (L-J) potential were adopted for bonding attraction and non-electrostatic interaction, respectively. They estimated the theta transition point and accounted for the conformational results of Dobrynin *et al.*[2] consistently acquired with variations of the monomer charge fraction.

The purpose of the present study lies on a development of the efficient hybrid architecture of MD and MC scheme to quantitatively predict the microstructural properties of polyelectrolytes by modifying the previous algorithm reported by Micka and Kremer.[7] Our scheme uses the Langevin dynamics and the off-lattice pivot algorithm to properly equilibrate both scales of short and long-ranges. We are faithfully guaranteed both rightness and effectiveness of the newly developed algorithm by comparing with the previous results.[7,11] Simulation results on the conformational properties of polyelectrolytes are presented according to the physicochemical variations of, *inter alia*, the Debye length and the Bjerrum length that we consider to be the important quantities for the experimental scientists.

It would be noted that an explicit treatment of counter-ion condensation originally proposed by Manning[12] has been studying as a recent work. Since this work is beyond the present study, we do not address more unambiguous consideration of the charging mechanism to describe the counter-ion condensation.

Hybrid Architecture of Molecular Dynamics (MD) and Monte Carlo (MC) Algorithm

MD Coupling to a Heat Bath. We used a standard velocity Verlet algorithm in order to integrate the equations of motion. Considering the frictional force and random force $\boldsymbol{\xi}_i(t)$, the equation of motion for monomer i is given by[6,13-15]

$$m\frac{d^2\boldsymbol{r}_i}{dt^2} = -\nabla\mathcal{H}_i - \Gamma\frac{d\boldsymbol{r}_i}{dt} + \boldsymbol{\xi}_i(t) \tag{1}$$

where m is the mass of monomer, $\boldsymbol{r}_i$ the position vector of i-th monomer, $\mathcal{H}_i$ the Hamiltonian of i-th monomer, and Γ the frictional coefficient that couples the monomers to the heat bath. The random force $\boldsymbol{\xi}_i(t)$ is related to the frictional coefficient *via* a fluctuation-dissipation theorem as, $\langle\boldsymbol{\xi}_i(t)\cdot\boldsymbol{\xi}_j(t')\rangle \equiv 6k_BT\delta_{ij}\delta(t-t')\Gamma$, assuming Gaussian white noise.[6,15] Here, k_B is the Boltzmann constant, T the absolute temperature, δ_{ij} the Kronecker delta, and $\delta(t\text{-}t')$ the Dirac delta function which shows the autocorrelation of the time scale.

The polyelectrolyte is represented as N freely-jointed beads-chain to take into account the excluded volume effect. The bonds between neighboring beads are described by the Hookean potential with harmonic springs. The Hamiltonian appeared in eq (1) includes the Hookean model and D-H (equivalently, Yukawa) potential, which yields

$$\mathcal{H} = \sum_{i=1}^{N-1}\frac{3k_BT}{2b^2}(\boldsymbol{r}_i-\boldsymbol{r}_{i+1})^2 + \sum_{i=2}^{N}\sum_{j=1}^{i-1}\lambda_B k_BT\frac{exp(-\kappa r_{ij})}{r_{ij}} \tag{2}$$

where $b=\sqrt{\langle\mathbf{b}^2\rangle}$ is the bond length between the adjacent monomers, r_{ij} the distance between i-th and j-th monomers, and the Bjerrum length λ_B(i.e., in dimensional, $e^2/4\pi\varepsilon k_BT$) is a measure of the strength of the electrostatic interaction. The dynamics of the solvent (i.e., water) is based on a continuum approach, and its dielectric constant ε is computed using a relative permittivity as 78.5 taken at 298 K. Although free ions are not included explicitly in the simulation, their effect is described *via* the dependence of the inverse Debye screening length κ (i.e., in dimensional, $\sqrt{e^2\sum_i Z_i^2 n_i/\varepsilon k_BT}$) on the electrolyte concentration. Here, e represents the elementary charge, Z_i the amount of charge on monomer i, and n_i the ionic concentration.

The second term of the right-hand side of eq (1) models a

frictional damping of the solvent, which is proportional to the temporal change of the position vector. The third one mimics the random collisions with solvent molecules.[15,16] The equation of motion is then integrated with velocity Verlet algorithm,[6,17] can be written

$$\left(\frac{dr}{dt}\right)^{n+1/2} = \left(\frac{dr}{dt}\right)^{n} + m^{-1}\frac{\Delta t}{2}\left[-\nabla\mathcal{H}(r^n) - \Gamma\left(\frac{dr}{dt}\right)^{n} + \xi^n\right], \quad (3)$$

$$r^{n+1} = r^n + \Delta t\left(\frac{dr}{dt}\right)^{n+1/2}, \quad (4)$$

$$\left(\frac{dr}{dt}\right)^{n+1} = \left(\frac{dr}{dt}\right)^{n+1/2} + m^{-1}\frac{\Delta t}{2}\left[-\nabla\mathcal{H}(r^{n+1}) - \Gamma\left(\frac{dr}{dt}\right)^{n+1} + \xi^{n+1}\right]. \quad (5)$$

MC Scheme with Off-lattice Pivot Algorithm. We employed the off-lattice pivot algorithm in MC simulations with the canonical ensemble. This method is to allow the simulation to be quite efficient for a single chain, and offers all possible self-avoiding walks conformation with equal probability.[6] We choose some site ω_k along the walk as a pivot point, and apply some symmetry operation of the lattice to the part of the walk subsequent to the pivot point. The proposed new walk is

$$\omega_i' = \begin{cases} \omega_i & for \quad 0 \le i \le k \\ \omega_k + \Xi(\omega_i - \omega_k) & for \quad k+1 \le i \le N \end{cases} \quad (6)$$

where Ξ is the chosen symmetry operation. In the off-lattice pivot move, a pivot point among the chain monomers is chosen at random, and three dimensional rotating angles are also determined randomly to elaborate the new conformation, as follows

$$\Delta \boldsymbol{r} = A(\alpha_1, \alpha_2, \alpha_3)[\Delta r_x, \Delta r_y, \Delta r_z]^T. \quad (7)$$

Here, A is the rotational transformation matrix that includes the sinusoidal functions of random rotation angles α_1, α_2, and α_3. After pivoting, a classical Metropolis algorithm[17] determines the adoption or rejection of the new conformation by comparing a screened Coulomb (i.e., Debye-Hückel) interaction energy.

Simulation Scheme and Runs. In the previous study, the local structure was initially equilibrated by 10^5 MD steps, and then the overall structure was relaxed by adding 5×10^4 pivot moves. And subsequently, both MD and MC were completely mixed to generate the final conformation *via* $1\sim3 \times 10^7$ steps. In the process of the hybrid of MD and MC proposed by Kremer and coworkers,[7,11] the MC pivot step rendering the initial bond stretching helps to generate the large-scale structure. However, we found that the random large-scale pivot moves surely result in a difficult procedure

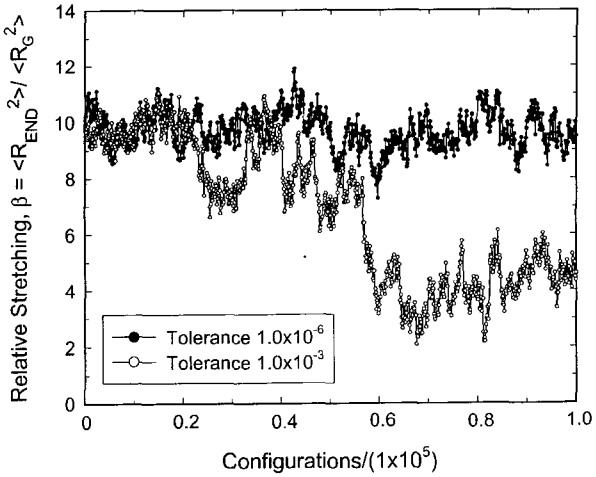

Figure 1. Characteristic mean square ratio of end-to-end distance and radius of gyration as the hybrid simulation proceeds for N = 128, b = 2.0, κ^{-1} = 100, and λ_B = 1.0, restarting from the equilibrium value. For the case of tolerance of 1×10^{-3}, equilibrium state is not sustained.

in finding an accurate equilibrium point. For the present simulations, the variables are nondimensionalized by the monomer diameter σ = 1.0 for length scale as well as the characteristic time $\tau = (m\sigma^2/\Lambda)^{1/2}$ for time scale at constant temperature $k_BT = 1.0\Lambda$, where both σ and Λ denote the L-J potential parameters.[6]

In Figure 1, we present two cases of totally different results obtained from different accepting tolerances for the pivot moves while the MD computation is running. In the process of MD steps, the MC computations are performed if the random number is smaller than the tolerance. Note that the equilibrium configuration can be more sustained as the tolerance decreases (i.e., narrow acceptance bandwidth). A coil-to-rodlike transition parameter β ($\equiv \langle R_{End}^2 \rangle / \langle R_G^2 \rangle$) estimated in Figure 1 involves the conformational information, where both the end-to-end distance and the radius of gyration will be explained in the next section. In Figure 1, we restarted the hybrid of MD and MC step with two accepting tolerances of MC pivot moves from the fully converged equilibrium state as an initial condition. This result presents that after equilibrium state achieved by MD computations, the MC off-lattice pivot step rather hinders the convergence. Therefore, we reasonably start with 10^3 MD steps to allow for initial bond stretching and the 10^4 pivot steps equilibrate the large-scale structure. Then pure MD time integration step of about $2 \times 10^5 \sim 10^6$ is carried for final conformation which corresponds to 1/10~1/50 configuration number of the previous study.[11]

Two initial conformations of the random walks and the totally stretched states are used to set for comparison, and then the equilibrium state is determined when both conformations finally produce the same β for several quantities. We performed each of 6 independent computations for each

of two initial conformations, from which total 12 independent states are acquired with statistical errors less than 4%. Our program yields the run time of about 5 hours on a Pentium III processor for each case.

Results and Discussion

Conformation Properties and Structure Factor. The characteristic quantities for the conformation of polyelectrolyte chains can be the end-to-end distance R_{End} and the radius of gyration R_G, defined as follows,

$$\langle R_{End} \rangle = \sqrt{\langle (\boldsymbol{r}_N - \boldsymbol{r}_1)^2 \rangle}, \tag{8}$$

$$\langle R_G \rangle = \sqrt{\frac{1}{N} \langle \sum_{i=1}^{N} (\boldsymbol{r}_i - \boldsymbol{r}_{CM})^2 \rangle} \tag{9}$$

where $\boldsymbol{r}_{CM}$ is the center-of-mass position vector. A characteristic relative stretching ratio β is 6 for the ideal chain with random walks, 12 for the totally stretched state, and a value around 6.3 for the self-avoiding walks. Figure 2 shows a relationship between β and the chain dimension N. As the number of monomers increases, a polyelectrolyte chain tends to stretch because once the chain length increases the screening effect decreases for the given value of Debye length. Our simulation results are in a good agreement with those of previous study.[7]

The structure factor represents an important microstructural information that gives all length scale data, and makes the theoretical prediction comparable to the experimental data.[3,7,18] Considering the scattering from two particles, the incident beam propagates along the vector $\boldsymbol{k}_i$ and the scattered beam along $\boldsymbol{k}_s$. The scattering wave vector $\boldsymbol{q}(\equiv \boldsymbol{k}_s - \boldsymbol{k}_i)$ has a magnitude $|\boldsymbol{q}| = 2|\boldsymbol{k}|sin(\theta/2) = (4\pi/\lambda)sin(\theta/2)$, where λ is the wavelength in the dispersion medium, and θ the scattering angle.[19] We can then define the spherically-averaged structure factor $S_{SP}(\boldsymbol{q})$ for the scattering wave vector $\boldsymbol{q}$ in the spherical coordinate, which is the Fourier transform of the pair correlation function $g(\boldsymbol{r})$, expressed as

$$S_{SP}(\boldsymbol{q}) \equiv \left\{ \frac{1}{N} \left| \sum_{i<j}^{N} \exp(-i\boldsymbol{q} \cdot (\boldsymbol{r}_i - \boldsymbol{r}_j)) \right|^2 \right\} = \frac{1}{N} \int d\boldsymbol{r} \exp(i\boldsymbol{q} \cdot \boldsymbol{r}) g(\boldsymbol{r}). \tag{10}$$

The spherically-averaged structure factor is eventually derived as a function of scattering wave number q, given by[3,18]

$$S_{SP}(q) = 1 + \frac{1}{N} \sum_{i,j}^{N} \frac{sin(qr_{ij})}{qr_{ij}}. \tag{11}$$

An important fact to be noted here is that the chain length dependency appears in the small q region as displayed in Figure 3. This is because the correlation between monomers increases with decreases of the wave number q, owing to the long wave length of scattering wave vector. To the contrary, the structure factor converges to unity because as the q increases it does not depend on the monomer correlation, which can easily be confirmed by eq (11). The rightness of our algorithm can be verified from a good agreement with the previous results.[7]

Screening Effect of the Solvent. In Figures 4 and 5, we investigate the screening effect caused by the salt and counter-ions in solvents. In the region of wave number q ranged 2×10^{-2} to 2, the $S_{SP}(q)$ function depends on the Debye length κ^{-1} with a constant slope, which is related to the chain conformations in terms of collapsed, totally

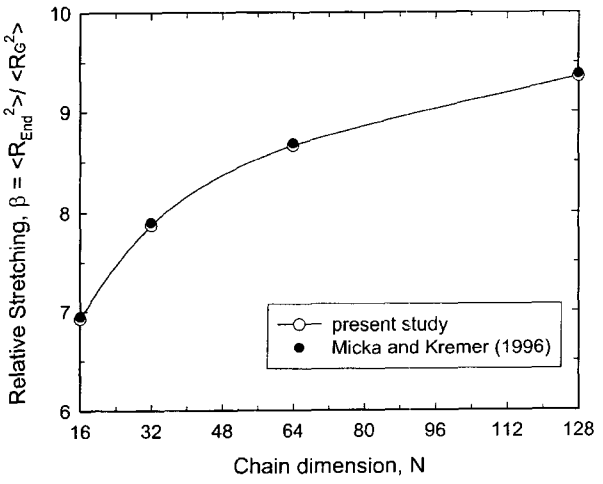

Figure 2. Characteristic mean square ratio of end-to-end distance and radius of gyration for different chain dimensions (N = 16, 32, 64, 128) with b = 2.0, κ^{-1} = 100, and λ_B = 1.0.

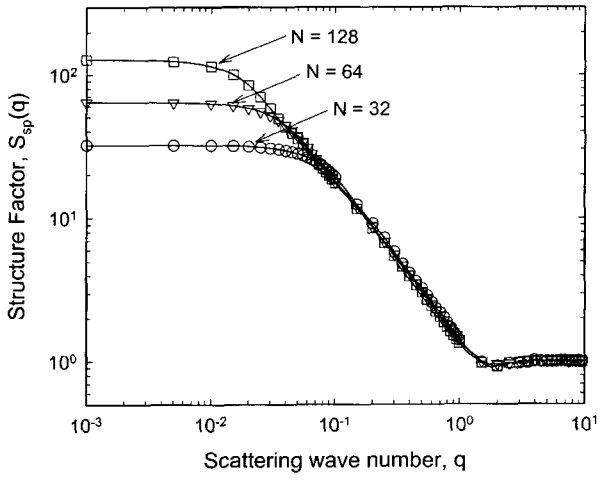

Figure 3. The comparisons of spherically-averaged structure factor at different chain dimensions (N = 32, 64, 128) with b = 2.0, κ^{-1} = 100, and λ_B = 1.0. Solid curves correspond to results of the present hybrid algorithm, and symbols indicate those of Micka and Kremer.[7]

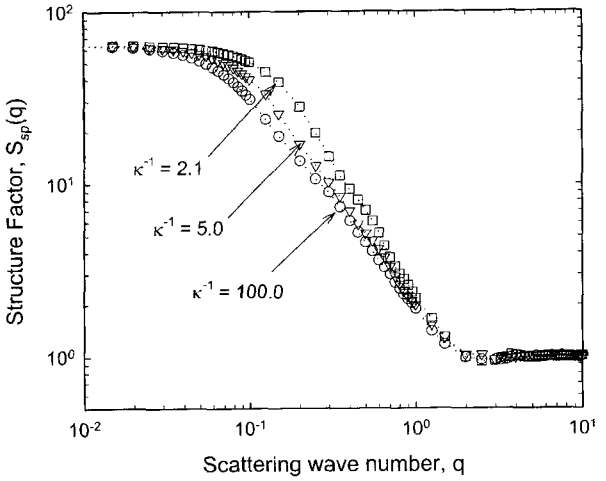

Figure 4. The variations of spherically-averaged structure factor at different Debye lengths κ^{-1}, with $N = 64$, $b = 2.0$, and $\lambda_B = 0.25$.

stretched, and intermediate states. On the exterior of this region of the q, however, structure factors do not depend on κ^{-1}. The predicted structure factor can properly be compared with the scattering experiments. When a magnitude of the slope between q and $S_{SP}(q)$ is small, a polyelectrolyte chain is expanded with the self-avoiding walks conformation in good solvent condition. As the slope increases a chain experiences the random walks in theta solvent condition that is a balanced state between the attraction and the repulsion, and ultimately the poor solvent condition with collapsed globular conformation is obtained.

Figure 5 visualized with a software POV-Ray Version 3.1 (cf., http://www.povray.org) provides the same trend as discussed above. As the screening effect decreases (i.e., larger value of κ^{-1}), a chain starts to elongate due to the strong repulsion, and finally forms a stretched equilibrium state.

Monomer Charge Effect. The structure factors for various Bjerrum lengths λ_B were estimated to investigate a relationship between the chain conformation and the charge of monomers. In Figure 6, as the Bjerrum length increases the magnitude of the slope between q and $S_{SP}(q)$ decreases due to the monomer-to-monomer repulsion. Figure 7 shows snapshots of the conformational structure with different Bjerrum lengths, and the almost spherical globule is observed in Figure 7(a). In cases of λ_B with 0.25 and 0.5, a long-range structure becomes elongated, with which local globules can also be found amongst polyelectrolyte chain. Finally, a chain becomes to the fully elongated state due to the stronger monomer-to-monomer repulsion when λ_B equals unity.

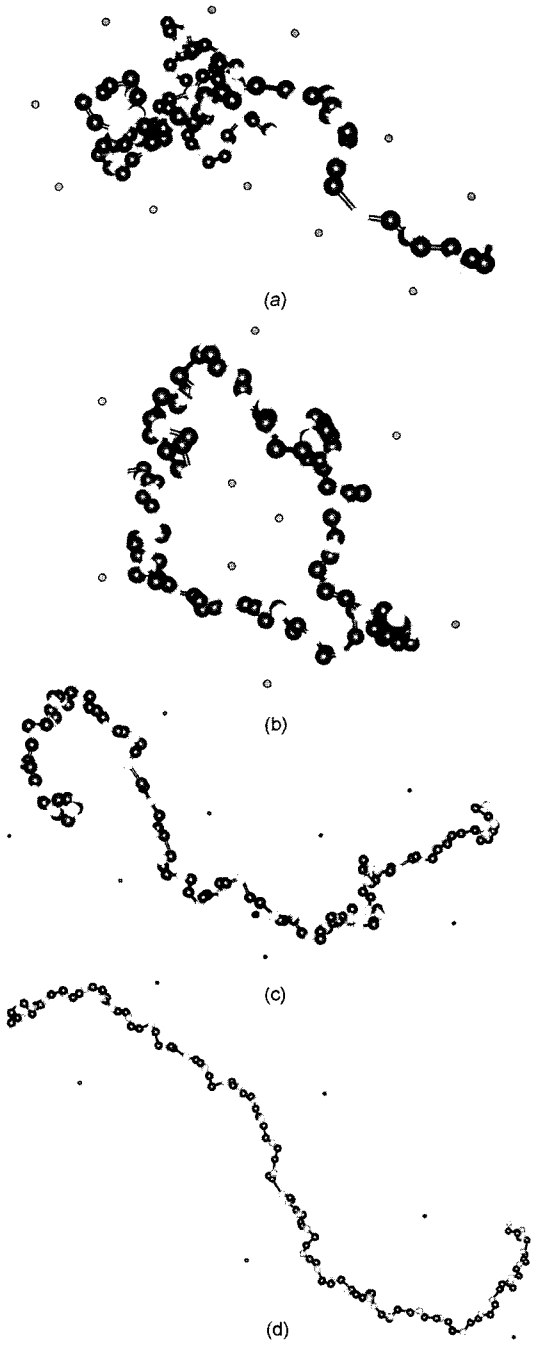

Figure 5. Snapshots of the equilibrium chain conformations at different Debye lengths of (a) $\kappa^{-1} = 2.1$, (b) $\kappa^{-1} = 5.0$, (c) $\kappa^{-1} = 20.0$, and (d) $\kappa^{-1} = 100.0$, with $N = 128$, $b = 2.0$, and $\lambda_B = 1.0$. Although all of the monomers are charged, gray-colored monomers are applied to clearly enhance 3-dimensional visualizations. The counter-ions are virtually indicated as small dark-gray spheres.

Conclusions

An efficient hybrid algorithm of MD and MC was developed to predict the polyelectrolyte conformation. In the present algorithm, the MC off-lattice pivot step was adopted just in early stage and then a pure MD step followed. As a consequence, we could reasonably exclude the unstable oscillations due to random large-scale pivot moves which caused a difficult procedure in the previous study. Comparing

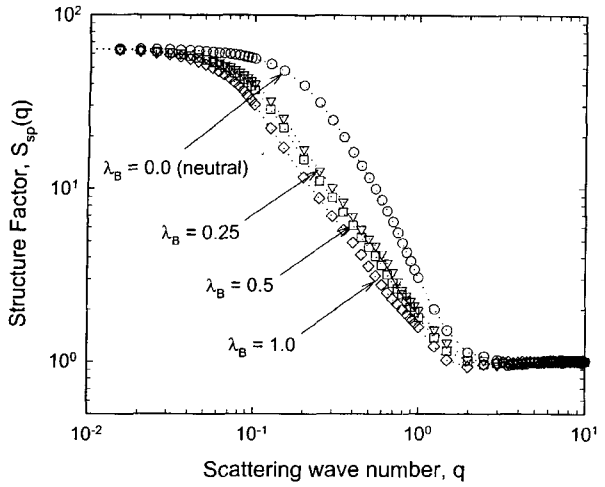

Figure 6. The variations of spherically-averaged structure factor at different Bjerrum lengths λ_B, with $N = 64$, $b = 2.0$, and $\kappa^{-1} = 5.0$.

with the previous scheme, it is evident that the computational configuration number is quite reduced, and a rightness of the algorithm is verified.

For a weakly charged polyelectrolyte in solvents, the freely-jointed beads and chain have been modeled by the harmonic spring potential coupled with D-H potential (cf., the solution of the linearized Poisson-Boltzmann equation). Simulation results of the polyelectrolyte conformation were achieved with various Debye length κ^{-1} and Bjerrum length λ_B. We view the present investigation as a promising first step, which we will extend to the problem of polyelectrolytes in confined spaces in the future.

Acknowledgement. This study was supported by the Basic Research Fund (Grant No. R01-2001-000-00411-0) from the KOSEF. M.-S. C. especially thanks to Dr. C. Holm and Director Professor K. Kremer at the Theory Group of Max-Planck Institute for Polymer Research at Mainz, for valuable discussions during the visiting research funded by the DFG as well as the KOSEF. Regarding the off-lattice pivot algorithm, the basic code developed by the Theory Group was employed in our program.

Nomenclatures

- A : rotational transformation matrix [-]
- b : monomer-to-monomer bond length [-]
- e : elementary charge [Coul]
- g : pair correlation function [-]
- $\mathcal{H}$: Hamiltonian [J]
- $\boldsymbol{k}$: wave vector [-]
- k_B : Boltzmann constant [J/K]
- m : dimensionless monomer mass [-]
- N : number of monomers [-]
- n_i : ionic concentration [1/m^3]

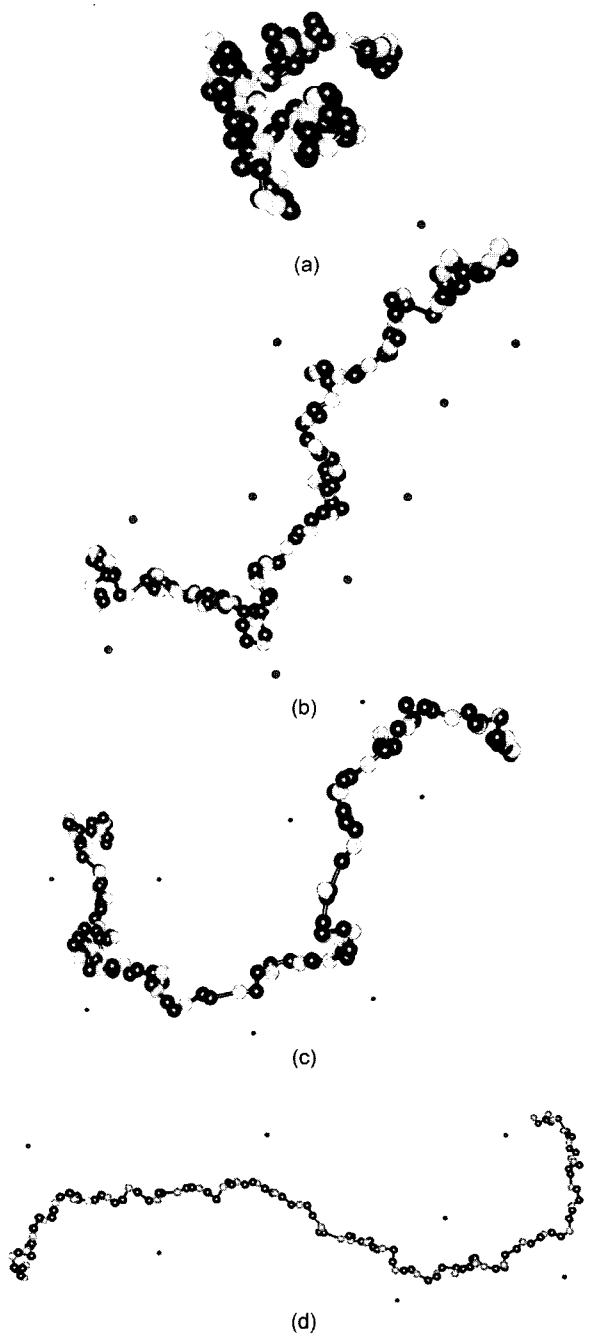

Figure 7. Snapshots of the equilibrium chain conformations at different Bjerrum lengths of (a) $\lambda_B = 0.0$ (neutral), (b) $\lambda_B = 0.25$, (c) $\lambda_B = 0.5$, and (d) $\lambda_B = 1.0$, with $N = 128$, $b = 2.0$, and $\kappa^{-1} = 100.0$. The coloring is as in Figure 5.

- q : scattering wave number [-]
- R_{End} : end-to-end distance [-]
- R_G : radius of gyration [-]
- $\boldsymbol{r}_{CM}$: dimensionless center-of-mass vector of polyelectrolyte chain [-]
- $\boldsymbol{r}_i$: dimensionless position vector of i-th monomer [-]

r_{ij} : distance between i-th and j-th monomers [-]
S_{SP} : spherically-averaged structure factor [-]
T : absolute temperature [K]
t : dimensionless time [-]
Z_i : amount of charge on monomer i [-]

Greek Letters

β : characteristic relative stretching ratio [-]
I : dimensionless frictional coefficient [-]
ε : dielectric constant or permittivity [$Coul^2/J \cdot m$]
θ : wave angle [deg]
κ : inverse Debye length [-]
Λ : L-J parameter of interaction energy [J]
λ : wave length in the dispersion medium [m]
λ_B : Bjerrum length [-]
ξ : dimensionless random force [-]
σ : L-J parameter of monomer diameter [m]
τ : characteristic time

Mathematical

δ_{ij} : Kronecker delta
δ : Dirac delta function

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