A Monte Carlo simulation of grafted poly(ethylene oxide) chains

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Abstract

Conformational changes of a simplified model of grafted poly(ethylene oxide) (PEO) chains were simulated using an off-lattice Monte Carlo model. A random-walk scheme was used in our simulations. The initial polymer structure was modeled with molecular mechanics and models of grafted polymer chains were built using programs developed in our laboratory. During the simulation, all bond angles and bond lengths were kept fixed while the dihedral angles of backbones were changed to search for energy-favorite conformations. Torsional energy, van der Waals interaction, and Coulombic interaction were considered. Periodic boundary conditions were implemented. In addition, the solvent quality was simulated implicitly by modifying the Lennard-Jones 12–6 van der Waals expression. Each PEO chain, 50-monomer long, was represented with a united-atom model. Eight series of simulations with varying solvent quality, simulation temperature, and Coulombic interaction were carried out. For each series, nine different initial grafting densities of grafted PEO chains were considered. Five different conformations were simulated at each grafting density. The calculated system energies, scaling properties, and atom density profiles were studied. Changes in solvent quality produced different structural behaviors. As the grafting density increased, there was a mushroom-to-brush transition, and the scaling property of average layer thickness was dependent on the grafting density. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene oxide); Poly(ethylene glycol); Monte Carlo simulation; Scaling; Surface grafting; Computer simulation; Solvent quality

1. Introduction

Polymer chains can be covalently attached to a solid surface by one end. The grafted chains form a mobile and flexible layer which contacts with other phases and grants the surface desired optical, electrical, rheological and chemical properties. With a layer of biocompatible polymer chains, a material can have a property such as preventing proteins and cells from adsorbing to the material's surface [1–3]. Poly(ethylene oxide) (PEO), a hydrophilic polymer, has been most widely used in surface grafting to make biocompatible materials. Due to the unique properties of the grafted PEO polymer, many theoretical and experimental studies have been done to study the structural and thermodynamic properties of the grafted polymer chains [4–8].

Computer simulations for studying structural properties of molecular systems can generate useful information. For studies of the static structural behaviors of grafted polymer chains, Monte Carlo (MC) simulation method is easy to implement. One of its interesting features is the rigidity or stiffness of polymer chains. Without the consideration of the rigidity, at a very low grafting density, the polymer chains may totally collapse. Another motivation of this study was to employ a more realistic model to simulate the grafted polymer chains. We used an all-atom model and a united-atom model with considerations of torsional energy and non-bonded interactions (van der Waals and Coulombic). For simulating the solvent quality, van der Waals expression was modified to include an implicit solvent layer in the simulation. Effects of simulation temperature on polymer structures were also studied.

2. Model and simulation procedure

2.1. Random-walk scheme

In our off-lattice MC simulation, the polymer layer consisted of polymer chains fixed at one end on a grafting surface and the remaining chains were free to move above the surface. Each chain was represented with either an all-atom model or a united-atom model depending upon the available computer power. The all-atom model included all of the atoms while the united-atom model was simplified with all hydrogen atoms united or combined to their host

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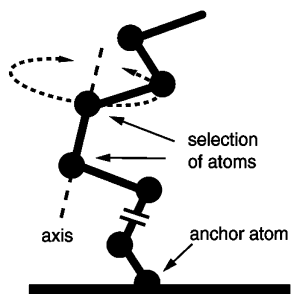 *E-mail address:* esp@omni.cc.purdue.edu (K. Park).

Fig. 1. Illustration of the MC random-walk scheme used in our study. Two bonded atoms were randomly selected and the bond was used as an axis. All the atoms above the upper picked atom up to the top of the chain were rotated around the axis. The amount and the direction of the rotation were randomly generated.

carbon or oxygen atoms. The positions and charges of the hosting C and O atoms were weighted with their implicit H atoms. If a hydrogen atom was part of the main chain (e.g. –OH at the end), it was reserved so that the overall chain structure was still maintained. The initial structures of all chains were the same and duplicated from a template chain. The template chain was built and optimized with a molecular modeling program so that the bond lengths and bond angles were kept at their energy-favored states. Atomic charges were assigned by the force field used. The chains were distributed uniformly in a lattice pattern on the grafting surface. The spacing distance (i.e. the distance between the neighbor anchors) and the number of polymer chains used in the simulation were specified before starting simulations.

The interaction potentials were obtained from AMBER [9]. Three energy terms were considered in our simulation. One was the torsional energy defined as:

$$E(\theta) = \tfrac{1}{2} K_{\theta,n}[1 - d\cos(n\theta)] \tag{1}$$

where θ was the torsional angle, $K_{\theta,n}$ was a constant (in kcal/mol), n was the periodicity of the potential, and d was the phase factor. Another two energy terms were van der Waals and Coulombic interactions. The van der Waals interaction was described with a Lennard-Jones 12–6 expression:

$$E_{\text{vdw}}(R_{ij}) = D_0 \left\{ \left[\frac{R_0}{R_{ij}} \right]^{12} - 2 \left[\frac{R_0}{R_{ij}} \right]^6 \right\} \tag{2}$$

where R_{ij} was the distance between two interacting atoms i and j, the parameters D_0 and R_0 were related to the types of the interacting atoms. The Coulombic interaction was defined as:

$$E_{\text{coul}}(R_{ij}) = \frac{Q_i Q_j}{\epsilon R_{ij}} \tag{3}$$

where Q_i and Q_j were the partial charges of atom i and atom j, respectively, and ϵ was the dielectric constant. In our simulations, ϵ was taken as the same value of R_{ij} in order to implicitly include the solvent screening effect of the

electrostatic interaction [10]. The cut-off distance to calculate the non-bonded interactions was 11 Å. No interaction was considered between the grafting surface and polymer chains.

Once the initial model was built, two procedures were carried out to simulate grafted polymer chains. Since the initial chains were linear, the first step was to relax the initial model. Then, the second procedure was to "cool" the relaxed structure down to an equilibrium state. The same random-walk approach was used for these two steps. During an elementary move, all the bond lengths and bond angles were kept unchanged while a torsional angle along one of the main chains was picked up randomly and assigned to a random value. The acceptance of this new torsional angle was judged with Metropolis MC sampling method [11]. Since all the chains were fixed at one ends, by changing the torsional angles while keeping the bond lengths and bond angles constant, the ergodicity was roughly achieved with ignorance of minor local fluctuations of the molecular system. Fig. 1 shows the basic algorithm of the random-walk scheme. First, a chain is randomly chosen. Then, two bonded atoms along the backbone are randomly chosen and the bond is used as an axis. All the atoms present above the selected upper atom are rotated around the axis. The degree of rotation is randomly determined except during the relaxation procedure where the new value of the torsional angle is randomly picked up from all energy-favored values. The direction of the rotation is also randomly determined. If the new position of any rotated atom is below the grafting surface or causes collisions with other atoms, this move is abandoned. In the second simulation procedure, the move is judged with the Metropolis method.

In simulations, the periodicity of all the torsional angles was 3. Thus, 0, 120 and 240° were the three energy-favorite configurations for a torsional angle. The initial model before starting a simulation had all the torsional angles set to 0°. During the first relaxation procedure, all possible torsional angles were randomly changed to one of 0, 120 and 240° values. The number of relaxation steps was roughly chosen in accordance with the number of all torsional angles along the backbones. This relaxing algorithm was similar to the rotational isomeric state (RIS) method [12]. After this procedure was done, the torsional energy was still zero but the non-bonded energies were unrealistically high. The same MC random-walk strategy was used to equilibrate the structure during the following procedure. The non-bonded energy was cooled down and the total energy was reduced to a limit allowed by the simulation temperature. During one MC move, a random value was added to or subtracted from a randomly picked torsional angle. The degree of the angle changed was dynamically adjusted according to the sampling success ratio which was controlled around 20% [13]. The dynamic adjustment method could effectively speed up the sampling procedure [14]. The periodic boundary conditions were used at both
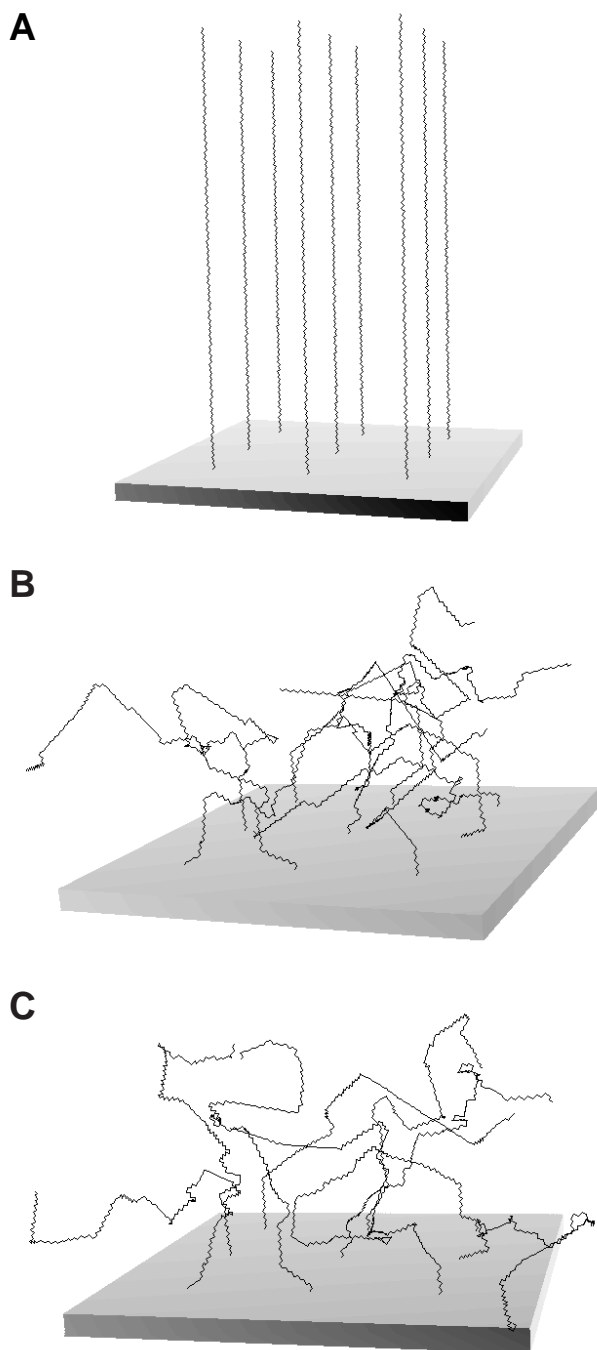
2.2. Simulation of solvent quality

The effect of solvent quality was implicitly handled in our simulation. In a good solvent, the polymer chains were regarded to interact with the solvent molecules more strongly than with other polymer molecules. Polymer chains cannot get closer to each other due to the presence of the solvent layer surrounding polymer chains. As the solvent quality increases, polymer chains have more difficulties to break the bound solvent layer. In this study, we modified the van der Waals expression to consider the effect of a solvent layer. As shown in Eq. (2), two parameters are used to describe van der Waals interaction with a Lennard-Jones 12–6 form. D_0 is the well depth of the interaction where the interaction eventually reaches the minimum, and R_0 is the corresponding distance between the interacting parties. When a solvent layer is present, the attraction is decreased while the repulsion is increased. Thus, we modified R_0 to include the solvent layer in order to simulate solvent quality. Given R_{sol} represented the "effective" thickness of the solvent layer, Eq. (2) was used to calculate van der Waals interaction if $R_{ij} > R_0 + R_{sol}$. If $R_{ij} \le R_0 + R_{sol}$, the following expressions were used:

$$E_{vdw}(R_{ij}) = D_0'\left\{\left[\frac{R_0 + R_{sol}}{R_{ij}}\right]^{12} - 2\left[\frac{R_0 + R_{sol}}{R_{ij}}\right]^{6}\right\} \quad (4)$$

and

$$D_0' = D_0\left\{\left[\frac{R_0}{R_0 + R_{sol}}\right]^{12} - 2\left[\frac{R_0}{R_0 + R_{sol}}\right]^{6}\right\} \quad (5)$$

Apparently, for a given R_{ij}, the modified van der Waals interaction between polymer atoms becomes greatly increased when a solvent layer is considered. The interacting atoms are repelled each other and the original van der Waals interaction (calculated using Eq. (2)) between polymer atoms is significantly reduced. The self-excluded volume of a polymer atom increases as well. This approach followed the Sariban's work where the solvent quality was varied by modifying the 6-term (i.e. the second term) in the Lennard-Jones 12–6 expression [15].

2.3. Implementation and simulation

The programs were written with ANSI C on a workstation (IBM RISC/6000). The package includes a building module, a simulation module, an analysis module, and a visualization module.

In our simulations of grafted PEO chains, the united-atom model of nine 50-monomer PEO chains was used mainly due to the limited computer resource. The initial structure was modeled with Quanta (Molecular Simulation Inc.). Charges were assigned by the force field used. Each model consisted of nine chains in a 3×3 layout with C ends fixed on the grafting surface. The spacing distances (i.e. the distances to an anchor's neighbor anchors) were equal. We studied eight series of different configurations

Fig. 2. Conformation snapshots of the simulation Series 7 (see Table 1). Nine grafted PEO chains were fixed at one ends in a 3×3 pattern. The spacing distance was 40 Å. (a) The initial model. (b) Conformation after the first simulation procedure. (c) Conformation after the second simulation procedure.

directions along the grafting surface. Seed numbers for the random-number generation were specified when starting the first and second procedures. An initial model of grafted PEO chains is shown in Fig. 2a. Fig. 2b and 2c shows conformations after the first and the second procedures, respectively.

Table 1
Configurations used in the simulations

Series index	Solvent layer[a] (Å)	Simulation temperature ($T^* = 1/kT$)	Coulombic interaction[b]
1	0.0	0.1	On
2	0.0	1.0	On
3	0.0	1.0	Off
4	0.0	3.0	On
5	0.5	1.0	Off
6	1.0	1.0	On
7	1.0	1.0	Off
8	1.5	1.0	Off

[a] Solvent layer, R_{sol}, is defined in Eqs. (4) and (5).

[b] "On" or "off" indicates whether the interaction was included in the total energy during simulations.

to investigate effects of solvent quality, simulation temperature, and atomic charges as well as the grafting density. Table 1 shows the configurations for all the series. Each series included nine different models with the spacing distances ranging from 20 to 100 Å at 10 Å intervals. Thus, the corresponding grafting density, σ, was calculated as 0.0025, 0.0011, 0.00062, 0.00040, 0.00028, 0.00020, 0.00016, 0.00012 and 0.00010, respectively. Each model was simulated five times by using different random-number generation seeds for the relaxation and the simulation procedures. The statistic properties were averaged over results from the five simulations. The first relaxation procedure generally carried out a few thousands of the MC moves. The second simulation procedure ran over one million MC moves. It was found that the total energy values became constant with minor fluctuations at the end of simulation procedures. Three simulation temperature values were used. To make it simple to input, a notation, T^*, was used to specify the temperature value. T^* is equal to $1/kT$ where k is the Boltzmann constant and T is the simulation temperature. The three values used were 0.1, 1.0 and 3.0. Four R_{sol} values were used, 0.0, 0.5, 1.0 and 1.5 Å. Simulations with and without the consideration of Coulombic interaction were also finished.

3. Results

3.1. Calculated energies of simulated PEO chains

There were three energy terms used in our simulations: torsional energy, van der Waals interaction, and Coulombic interaction. Fig. 3 shows these energy values plotted as a function of spacing distance. They were calculated from the final simulated structures. It is observed that when the spacing distance between the grafted PEO chains is small (i.e. the grafting density is high), the torsional energy values are small. The values go up and generally reach plateaus when the spacing distance increases. Apparently, at high
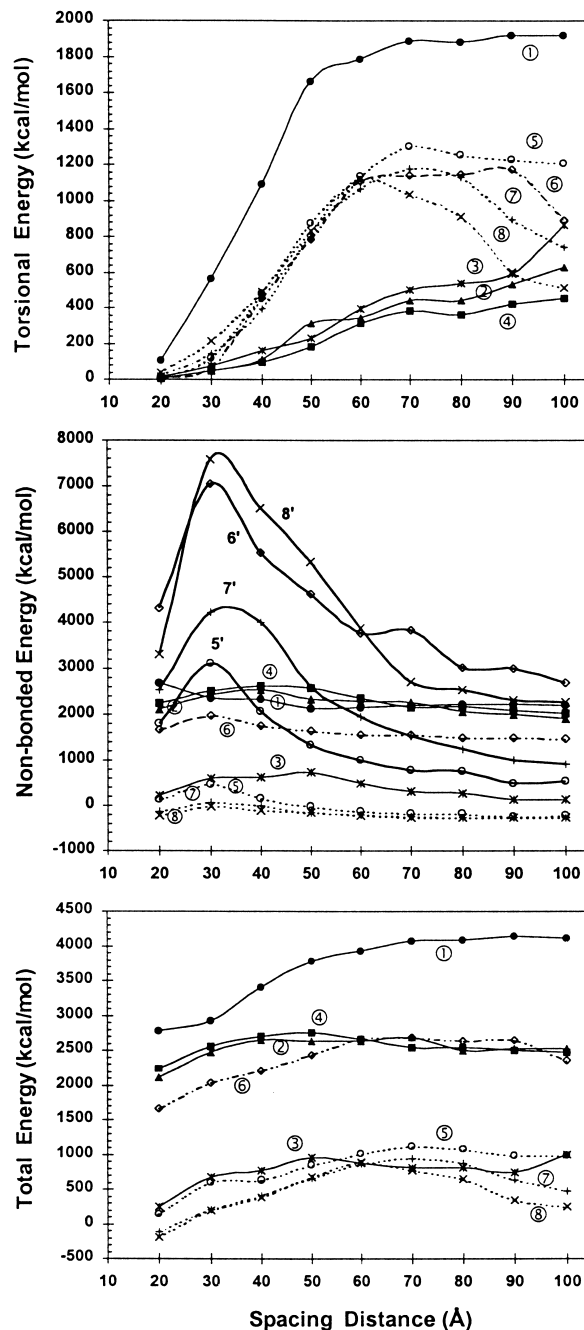

Fig. 3. Calculated torsional, non-bonded, and total energies as a function of the spacing distance of all simulation series. Each curve is marked with the series number in white circles as listed in Table 1. The four thicker, gray curves in the non-bonded energy figure, marked with the series numbers $5'$, $6'$, $7'$ and $8'$, show non-bonded energy values calculated with Eqs. (3)–(5).

grafting densities polymer chains do not have enough free space to fluctuate away from the initial conformations where all torsional angles are in their lowest-energy states. When the grafting density decreases, the torsional angles can move far away from the lowest-energy states and the energy values become increased. When the grafting density decreases to a point where the space does not limit the fluctuation of the torsional angles, the energy values stay
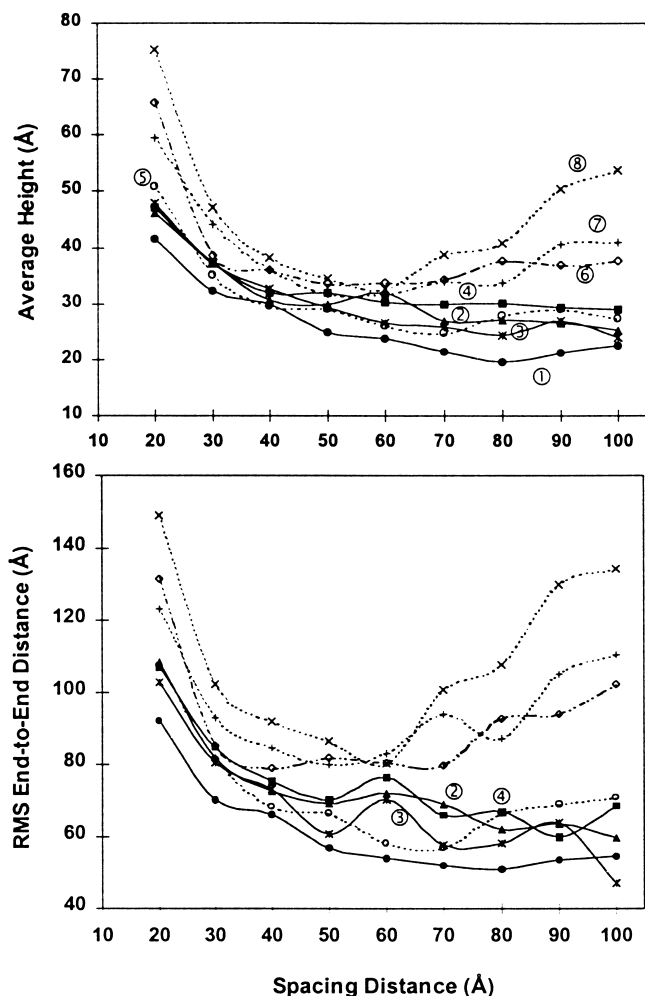
Fig. 4. Average height and root mean square (RMS) end-to-end distance of grafted PEO chains versus spacing distance. Each line is marked with the series number as listed in Table 1.

relatively constant. However, it is interesting to see that the torsional energies of the series with the solvent layers considered (i.e. Series 5–8) drop down after reaching maximum values at about 70 Å. The thicker the solvent layer, the larger the energy value drops. One possible reason could be the balance between the van der Waals interaction and the torsional energy. At a very low grafting density, when a thick solvent layer was simulated, the inter-chain van der Waals interactions became less important than the intra-chain interactions. To balance the increase in intra-chain interactions, the torsional energy had to decrease to keep the total energy remain the same. From Fig. 3, it is seen that the torsional energy curves can be roughly divided into three groups according to their values. The first group is for the series with $T^* = 0.1$ (i.e. Series 1). The second group is for those series with the solvent layer considered (i.e. Series 5–8), and the third group is for the series without the solvent layer considered (i.e. Series 2–4). A high simulation temperature, or a low T^*, causes an increase of the equilibrium thermoenergy. In addition, Fig. 3 shows the increase

of torsional energy of the second group caused by the effect of solvent layers.

The non-bonded interaction values of all simulation series are shown in Fig. 3. Four more curves (marked with the series number prime, i.e. $5'–8'$) are also shown in the non-bonded energy curve in Fig. 3. They were values calculated with the modified van der Waals equations (Eqs. (4) and (5)) with consideration of the solvent layer. The corresponding van der Waals energies that were calculated with Eq. (2) from the same final structures were much lower. The curves of total energy values did not change much as the spacing distance increased. The grafting density shows a very weak relationship with the non-bonded energy in simulations. It can be seen that one factor causing the difference among the curves is the consideration of Coulombic interaction. Another factor is the effect of the solvent layer. The effect of the solvent layer or solvent quality, however, is much weaker than the effect of Coulombic interaction. It is interesting to see that the simulation temperature did not have any effect on the values of non-bonded interactions. Moreover, the four curves of non-bonded interactions calculated with Eqs. (4) and (5) of the systems with the solvent layer have similar shape and trend.

Fig. 3 also shows the total energy values of all eight series of simulations. Of those systems where the solvent layers were considered, the values of van der Waals interaction calculated with Eq. (2) were used to draw the curves. Apparently, the eight curves in Fig. 3 can be divided into three different groups with close values. The first group has one curve with $T^* = 0.1$ (i.e. Series 1). The second group consists of three curves (i.e. Series 2, 4 and 6) where the systems were charged (i.e. Coulombic interaction was considered). These three curves have different simulation temperatures or different solvent quality. The third group has four curves (i.e. Series 3, 5, 7 and 8) where none of them was charged while solvent layers considered were different (0.5, 1.0, 1.5 or none). The total energy values of the polymer systems were affected by simulation temperature and Coulombic interaction. The solvent quality seems to have a minor effect on the total energy value. In addition, the grafting density affects the total energy but its influence is much weaker than the influences by the simulation temperature and Coulombic interaction. Given the size of the system simulated and the number of simulations for each model, some energy fluctuations were probably unavoidable.

3.2. Scaling properties and effect of solvent quality

Fig. 4 shows the average height and root mean square (RMS) end-to-end distance as a function of the spacing distance. Average height was calculated from height values of all atoms. End-to-end distance was the average height of free ends of polymer chains. It is shown that the polymer chains are more stretching at the higher grafting density than at the lower density. The heights of most of the simulated
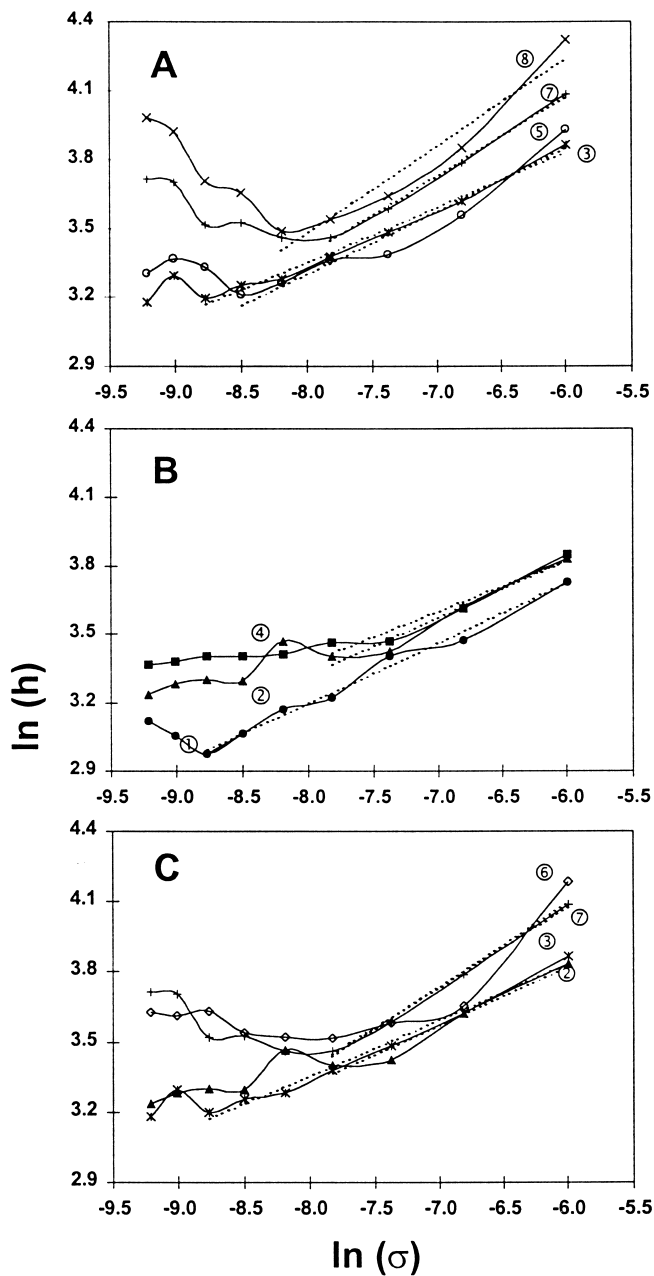
Fig. 5. ln(height) as a function of ln(grafting density). Each line is marked with the series number as listed in Table 1. (a) Effects of solvent quality; (b) simulation temperature; and (c) atomic charges on polymer structures are shown.

polymer chains remain almost constant at low grafting densities (i.e. from Series 1 to 5). The systems with $R_{sol} = 1.5$ and $R_{sol} = 1.0$ (i.e. Series 7 and 8) have interesting height profiles: when the grafting density becomes very low, the chains stretch again. This may be due to the increase in the share of the intra-chain van der Waals inter-action in the total energy values. Nevertheless, if the series with $R_{sol} = 1.5$ (i.e. Series 8) in Fig. 3 is assumed to be an extreme case and all other series are considered, one can observe the transition of the chain structures from a brush geometry to a mushroom geometry. When the grafting
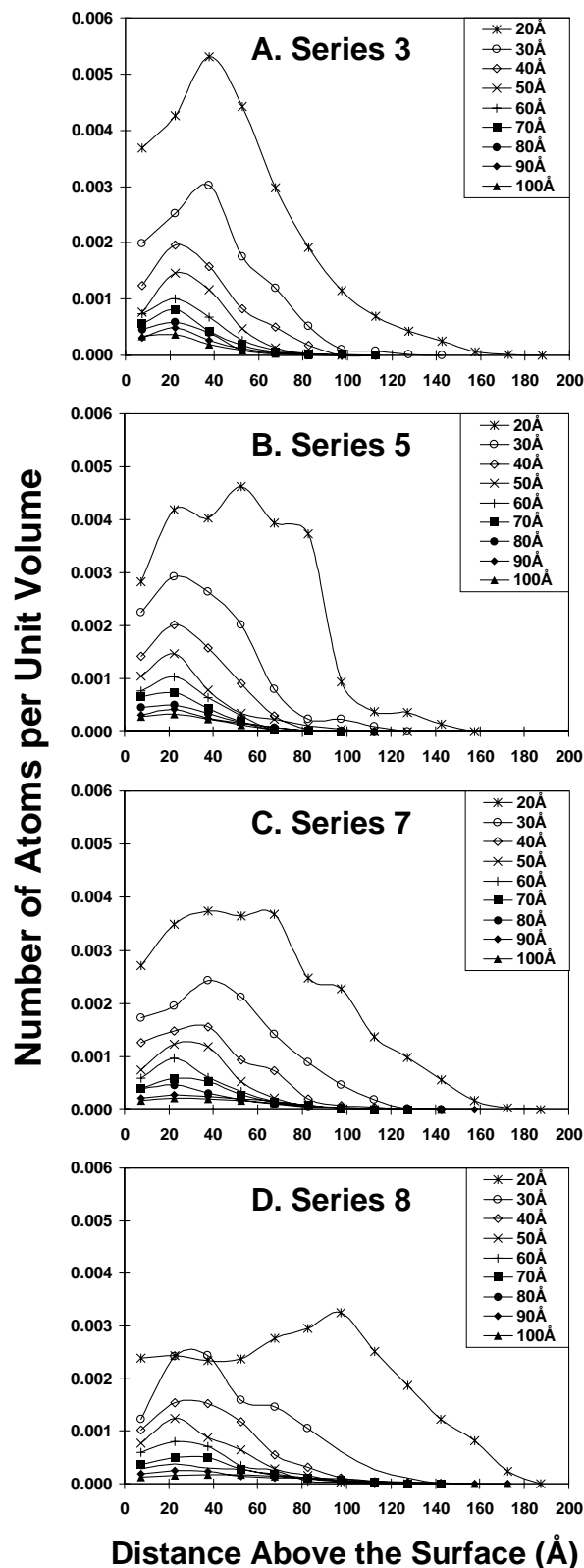

Fig. 6. Density profile versus the grafting density showing the effect of solvent quality.
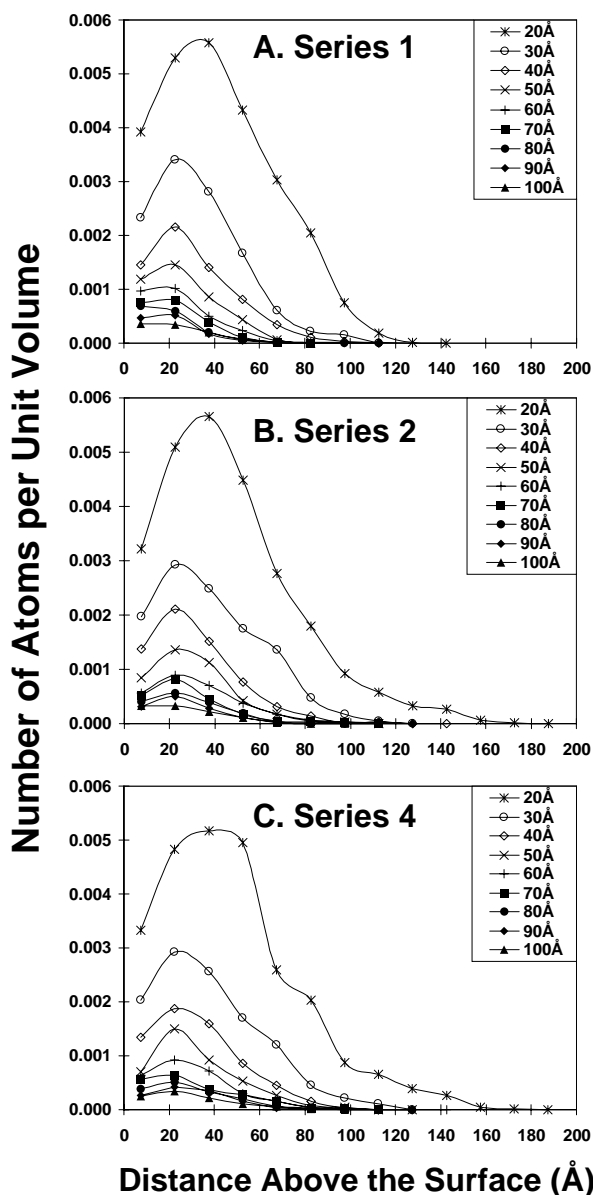
Fig. 7. Density profile versus the grafting density showing the effect of simulation temperature.

Four series of simulations with varying solvent layer thickness (0.0, 0.5, 1.0 and 1.5 Å) are plotted in Fig. 5a as $\ln(h)$ versus $\ln(\sigma)$ (i.e. Series 3, 5, 7 and 8). The linear curve fitting was done at the brush regime of all four series. The slopes calculated from the linear curve fitting are 0.38, 0.34, 0.27 and 0.24 for the series with $R_{sol} = 1.5$, 1.0, 0.5 and 0.0, respectively. The system of grafted chains with $R_{sol} = 1.0$ shows the scaling property, as predicted by the scaling theory and SCF studies in good solvents. In addition, it shows that the thicker the solvent layer, the stronger the dependence of the polymer height on the grafting density. At least in the range of grafting densities we have studied, if $R_{sol} = 0.0$ is used to represent a poor solvent (e.g. Series 1, 2 or 3), the strong dependence of polymer thickness on grafting density was not observed. Since the shortest spacing distance in our study is 20 Å, or $\sigma = 0.0025$, we believe that the grafted density is still very small to reach the stronger scaling regime in a poor solvent. It appears that the effect of self-excluded volume does not play an essential role in determining the chain structures in our simulation.

Effect of simulation temperature on the scaling property of the chain height was studied. Three series of simulations with $T^* = 0.1$, 1.0 and 3.0 are plotted in Fig. 5b as $\ln(h)$ versus $\ln(\sigma)$ (i.e. Series 1, 2 and 4). Coulombic interactions were included and no solvent layer was considered in the simulations. Linear curve fitting was carried out on the brush regime of the three curves. The slopes are 0.26, 0.25 and 0.22 for the series with $T^* = 0.1$, 1.0 and 3.0, respectively. Although the size of scaling regimes is different for the simulations with different simulation temperatures, the simulation temperature has a minor effect on the chain height scaling property. In addition, four curves of $\ln(h)$ versus $\ln(\sigma)$ in Fig. 5c (i.e. Series 2, 3, 6 and 7) show the effect of Coulombic interaction. Linear curve fitting was carried out on the brush regime of the three curves. The slopes are 0.25, 0.24, 0.36 and 0.34 for the series 2, 3, 6 and 7, respectively. Two pairs of series have the same simulation temperature or solvent layer thickness except the Coulombic interaction. For the pair with $T^* = 1.0$ and $R_{sol} = 0.0$ (i.e. Series 2 and 3), the inclusion of Coulombic energy in the simulations did not change the scaling property much. Neither did another pair where $T^* = 1.0$ and $R_{sol} = 1.0$ (i.e. Series 6 and 7).

3.3. Structure of the grafted chains

Structural properties of grafted polymer chains were studied by plotting the number of atoms per volume as a function of the distance above the grafting surface. Fig. 6 illustrates the atom density profiles of four series of simulations with focus on the effect of solvent layer (i.e. Series 3, 5, 7 and 8). Each series has nine configurations with varying spacing distances or grafting densities. In general, most of the profile curves have a parabolic shape with a depletion zone close to the grafting surface and a smooth tail. When the grafting density decreases, the shape of a profile tends to

density is low, the height of a polymer layer is independent of the grafting density. This is the mushroom regime. When the grafting density increases, the height increases as well. This is the brush regime. This transition has been observed in experimental studies [16–19] and in simulation studies [6,20,21]. Moreover, Fig. 4 indicates that the simulation temperature and consideration of atomic charges have minor effects on the overall structures of grafted polymer chains compared with the effect of solvent quality. At high grafting density, the polymer chains with the solvent layer considered stretch stronger than those without solvent layer considered. It seems that simulating the solvent quality by our method can mimic the structural behaviors in a solvent with varying quality.
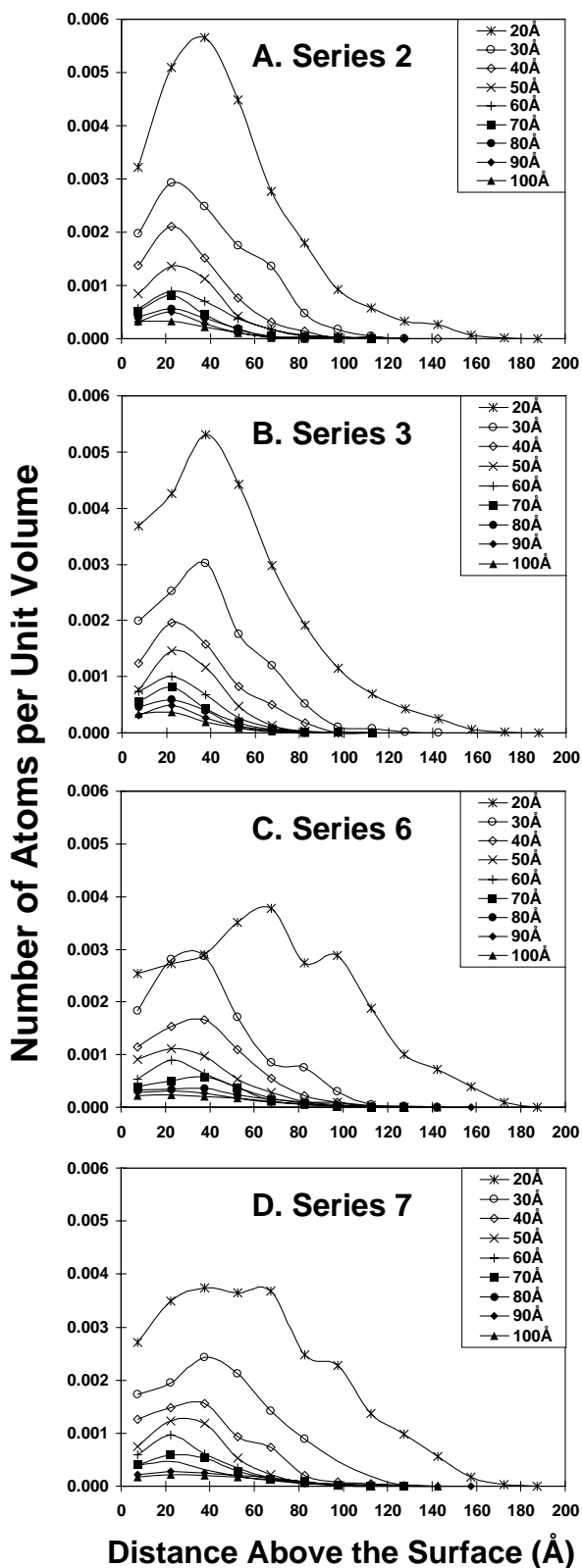
Fig. 8. Density profile versus the grafting density showing the effect of atomic charges.

drop slowly with a very long smooth tail extended as far as the profile of a higher grafting density. This observation is consistent with the experimental results by Auroy and Auvray [22]. In addition, no collapse has been observed for any system at the very low grafting density. The effect of solvent layer is shown in the figure. When R_{sol} increases from 0.0 to 1.5 Å as shown from Fig. 6a–d, the main body of the density profile at $\sigma = 0.0025$ (i.e. spacing distance is 20 Å) tends to be lower and wider, and, the tail becomes much linear. The average height of grafted chains increases and chains are adapted to more stretched conformations when the solvent layer becomes thicker. Nevertheless, the effect of the solvent quality has a small effect on the profile at $\sigma = 0.0011$ (i.e. spacing distance is 30 Å). For even lower grafting densities, the overall shapes of the density profile are very similar regardless of the solvent quality.

Fig. 7 shows three density profiles at different simulation temperatures ($T^* = 0.1$, 1.0 and 3.0, i.e. Series 1 in Fig. 7a, Series 2 in Fig. 7b, and Series 4 in Fig. 7c). These three simulation series had no solvent layer considered but had Coulombic interaction included in the calculation of chain energies. In Fig. 7, all the profiles have a parabolic body with a depletion zone close to the surface and a smooth tail. The corresponding curves of high grafting densities show similar shapes, and the curves of low grafting densities have almost the same shapes. Given the fluctuations of simulations, the simulation temperature shows no significant effects on the atom density profiles.

The effect of atomic charge on the density profile is shown in Fig. 8. Two simulations were run without the Coulombic interaction considered (i.e. Series 3 and 7 in Fig. 8b and 8d, respectively) and another two with the Coulombic interaction considered (i.e. Series 2 and 6 in Fig. 8a and 8c, respectively). The only difference was the solvent layer: Series 2 and 3 (Fig. 8a and 8b) had no solvent layer considered, while, Series 6 and 7 (Fig. 8c and 8d) had the solvent layer thickness taken as 1.0 Å. The simulation temperature was the same for these four series. When comparing atom density profiles of Series 2 in Fig. 8a with Series 3 Fig. 8b, corresponding curves look similar with some minor differences at high grafting densities. Likewise, when comparing Fig. 8c with Fig. 8d, the overall shape of corresponding curves look similar although curves with 20 and 30 Å show some difference. Therefore, inclusion of Coulombic interaction in simulations did not affect the overall conformations of grafted PEO chains.

4. Discussion

From results of our simulations, we found that most of atom density profiles had a parabolic body with a depletion zone and a smooth tail. The solvent quality affected

significantly the density profiles at high grafting densities. In a good solvent, the body of density profile was lower, wider and the tail was linear than those in a poor solvent. These results indicate that the grafted PEO chains tend to strongly stretch in a good solvent when the grafting density is high. This was observed by many experiments such as neutron reflectivity studies [5,16,23] and small-angle neutron scattering (SANS) of grafted or adsorbed polymer chains [22,24–29]. Our simulations also showed that the solvent quality affected the scaling property, $h \propto \sigma^{\nu}$, where h is the layer thickness, and σ is the grafting density. In a good solvent, the scaling behavior was in a good agreement as predicted by other theoretical and experimental studies. The scaling theories [30,31] and self-consistent-field (SCF) studies [32–35] indicated that in a good solvent h is proportional to $N\sigma^{1/3}$ (N is number of monomers per chain). In θ-or poor solvents, although inconsistencies can be found among various theoretical studies and experiments of grafted systems, a general observation was that h had a stronger dependency on σ than in good solvents (i.e. $\nu > 1/3$). Some studies showed that in a θ-solvent, h was scaled as $N\sigma^{1/2}$ [34]. Our results indicated that when the solvent layer thickness was 1.0 Å, ν values were close 1/3 (i.e. 0.36 for Series 3 and 0.34 for Series 4). However, in a poor solvent, the dependence of chain height on the grafting density was weaker than results of relevant SCF studies and simulations. When no solvent layer was considered in our simulations, ν values were close to 1/4, far smaller than 1/2. Interestingly, a recent experiment of tethered chains in good solvents reported the scaling representation at very low grafting densities [16]. The layer thickness was proportional to $\sigma^{0.22}$ rather than $\sigma^{1/3}$. It appears that the scaling property of layer thickness versus grafting density is dependent on the grafting density. The dependency can be affected by solvent quality, polymeric system, etc. This grafting density dependency can also be observed from the transition from a mushroom regime to a brush regime of structures of grafted chains. In the current regime of grafting density we studied, the series without consideration of solvent layer did not reach the stronger scaling regime where the effect of self-excluded volume dominated. Given a grafted polymer system at very low grafting densities, the solvent quality has a minor role in affecting the structures of grafted chains. When the grafting density is higher, the effect of solvent quality is much stronger. A molecular dynamics study reported that there were two scaling regimes of grafted polymer chains [20]. When the grafting density, σ, was increased to the second regime, the polymer thickness, h, scaled as $\sigma^{1/2}$ rather than $\sigma^{1/3}$ in the first regime. One neutron reflectivity study showed a mushroom-to-brush transition in a good solvent caused by varying the grafting density [17]. A similar observation was made with dynamic light scattering [18] and contact angle measurement with varying chain lengths [19]. The lowest grafting density we studied was 0.0001. At this grafting density, our results showed that the PEO chains were still stretching out and different solvent qualities affected chain structures as shown in Fig. 4. This may be due to consideration of the rigidity of grafted chains in simulations.

It was noticed that the rigidity of polymer chains was very important. Its effect could be observed from the percentage of torsional energy in the total value in the simulations. Without consideration of the rigidity, polymer chains could totally collapse at a low grafting density. In fact, from Fig. 3, it is seen that when the solvent quality is considered, the non-bonded energy calculated with Eqs. (2) and (3) is close to zero if no Coulombic interaction is included. The total energy of the system is mainly attributed by the torsional energy term. Obviously, without consideration of the rigidity, a large shift of total energy could result in significant changes of molecular structures.

It was shown that effects of simulation temperature and consideration of Coulombic interaction were insignificant on structures of grafted PEO chains in our simulations. The role of the simulation temperature in our simulations only affected the Metropolis sampling ratio or total energy. The higher the simulation temperature, the larger the total energy a system could have. In addition, inclusion of the Coulombic interaction into calculation of total energy had minor effects on chain height, scaling behavior, and density profile. Actually, since the distribution of the atomic charges along a PEO chain was uniform and the net value was zero, the consideration of Coulombic interaction just increased the total energy value.

However, Cook et al. reported that the increase in temperature or pressure leads to the decrease in solvent quality and thus, the behavior of PEO chains in water is dramatically affected [36]. They suggested that the hydrogen bonding between water molecules and PEO monomers is very sensitive to the temperature or the pressure. This implies that our solvent-layer model is inadequate without consideration of the temperature dependency. More efforts are needed to improve the model to simulate PEO chains in water.

It is noticed that a few density profile curves at $\sigma = 0.0025$ (i.e. spacing distance is 20 Å) in Figs. 6b and 8c do not have the smooth parabolic shape as others. One possible reason is the rather small size of PEO models and limited number of simulations for each model. There were only nine chains in one model and only five different conformations were averaged for one model. If the grafting density was very high, a polymer chain could interact with its mirror due to the usage of periodic boundary conditions. This may have resulted in biases of simulation results. Even if there were only nine chains in a model, the computation of simulations reported here required lengthy calculations. Increased computer power in the near future will allow simulations of more and longer polymer chains to gain more accurate pictures of conformations of grafted chains.

5. Conclusions

Dependency of the scaling property of the polymeric layer thickness (i.e. $h \propto N\sigma^y$) on the grafting density is related to the transition from a mushroom regime to a brush regime. Although the dependency has different expressions depending on the solvent quality, average heights and distributions of grafted chains are significantly affected by the grafting density. By considering the rigidity, at very low grafting densities, polymer chains are not collapsed on the grafting surface. In addition, our results indicate the solvent quality can affect conformations at a low grafting density, and, the intra-chain van der Waals interactions play the key role. Simulation temperatures and Coulombic interaction have only minor influence on the structural behaviors of grafted PEO chains but the improvement is needed to consider the temperature dependency of the solvent layer.

Acknowledgements

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