

Parallel Computing Properties of Tail Copolymer Chain

Hong Li^{1,3}, Bin Gong¹, He-Bei Gao^{*2}, Chang-Ji Qian³

¹School of Computer Science and Technology, Shandong University, Jinan, P. R. China

²Department of Computer, Wenzhou Vocational and Technical College, Wenzhou, P. R. China

³College of Physics and Electronic Information Engineering, Wenzhou University, Wenzhou, P. R. China

*Corresponding author, e-mail: bogolyx@163.com

Abstract

The properties of a AB diblock copolymer chain are calculated by Monte Carlo methods. Monomer A contacting to the surface has an adsorption energy $E=-1$ and monomer B $E=0$. The polymer chain is simulated by self-avoiding walk in simple cubic lattice. The adsorption properties and the conformation properties of the polymer chain are computed by using message passing interface (MPI). The speedup is close to linear speedup by parallel computing independent samples.

Keywords: parallel computing, self-avoiding chain, polymer, simulation

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1. Introduction

The motive of computer-generated is that people want to invent a machine used for scientific computing. In past sixty years, the computer has experienced rapid development with Moore's Law. The computing performance is double for the number of transistors doubling every 18 months. In the last 20 years, high-performance computing can be researched with the developments of parallel computing hardwares and software technologies [1-3]. High-performance computing is used to solve larger computing problems or to get more accurate solutions in the area of natural sciences and engineering. The computing of scientific problems becomes an increasingly important field in bioinformatics, materials science, fluid dynamics, drug design, computational chemistry, meteorology and so on [4-7]. To solve these problems only by the theoretical analysis and experiments has been difficult in dealing with the amount of data and the complexity of mechanism. Computer simulation can get the desired result on many specific problems, or be used to replace the physical experiment. High-performance computing is to develop and to apply mathematical modeling, data analysis, computer simulation technology for many applications. Therefore, we can extract useful information from the vast amounts of data with the large-scale computer simulation technology. Computational science is an interdisciplinary science of many application areas(such as physics, chemistry, or engineering et al.), which often applies high-performance computers to improve advanced theoretical and technical level in the individual science [1-5].

Computing theory and modeling of polymer is an important branch of polymer with the development of computer science. The polymer chain adsorbed at the interface becomes a hot research topic in the polymer and biological science [7-11]. The polymer is concatenated by a large number of the same structure unit. The linear chain is a simplified model commonly used for a polymer. Polymer chain has various conformations due to the constantly changing shape by the thermal motion of the molecules. The conformation of polymer chain at some time is completely random. Therefore there are very large number of polymer chain conformations for the molecular weight is often very large. No precise expression of partition function can resolve for long polymer chain. So conformational statistics of a single polymer chain is a complex computational problem. Then the simulation of polymer usually requires long computation time. In recent years, parallel computing is often the best choice, for serial computing can only be limited to calculate the short chain or local nature. The design of efficient parallel programming has been well established in scientific computing for many years. The static and dynamic properties of polymer chain can be obtained by parallel Monte Carlo simulations [12-14].

Computer simulations often require a large amount of calculation. With the cluster system becoming increasingly popular, parallel computing is often used for computer simulation

[12-14]. In order to effectively use the cluster, the problem is decomposed into a number of parallel computing portion. Each part should be independent and load ballancing as possible. In order to obtain a parallel computing, we select message passing interface (MPI) to achieve high performance.

In this paper, we simulate a single AB copolymer chain tethered to the surface by using parallel programming technology. We obtain nearly linear speedup by parallel computing the independent samples. This paper is organized as follows. The simulation method and a brief description of parallel computing properties of diblock copolymer are described in Section 2. Results and discussion are presented in section 3. Finally, our work of this paper is summarized in Section 4.

2. Research Method

The simulation system is often using the simple cubic lattice $L \times L \times L$. The monomer coordinate in chain (x, y, z) is valued in the grid with lattice length unit. A flat surface is placed at $z = 0$ which is impenetrable for polymer chain. Monomers of chain are all located above the surface ($z > 0$) and periodic boundary conditions are performed in x, y direction [3, 13].

Polymer chain is simulated by the self-avoiding walk (SAW). A chain is made up of N monomers consecutively linked with fluctuating bond length from 1, $\sqrt{2}$ and $\sqrt{3}$ unit. The bond between successive monomers in chain can be taken from the set $\{(1, 0, 0), (1, 1, 0), (1, 1, 1)\}$ by symmetry operations in the simple cubic lattice sapce. Each monomer occupies one unit in the grid lattice. The first monomer is fixed at the position $(0, 0, 1)$ which contacts to the center of flat surface $(0, 0, 0)$ and can't leave this position.

Diblock copolymer is a simple example of two-letter copolymers made up of two different monomers, marked by letters A and B. Monomer A is attractive to the surface, but monomer B is repulsive to the surface. Every monomer locating at layer $z = 1$ is contacting with the surface which is assigned an interaction energy $-E$. Monomer A contacts to the surface with a constant adsorption energy $E = -1$, but monomer B $E = 0$.

2.1 Chain Generation Method

The initial state of polymer is generated by self-avoiding walk which never visits the same lattice twice on the graph. The polymer is produced by walking step-by-step. An N -step self-avoiding walk is an ordered sequence of ($N+1$) monomers in polymer. The coordinates of the i th monomer, is marked as $(x[i], y[i], z[i])$ for $i = 0, 1, \dots, N$. The first monomer $(x[0], y[0], z[0])$ is located at the place $(0, 0, 1)$. On the simple cubic lattice, there are 6 nearest-neighbor sites on the primary lattice $\{(0,0,1), (0,0,-1), (0,1,0), (0,-1,0), (1,0,0), (-1,0,0)\}$. Each attempted walk involves a trial chosen one of the direction at random..

A 3D array $g[L][L][L]$ is used to flag the state of the lattice space. A lattice unit can only be occupied by a monomer of chains, for example the number 0 is for empty lattice, 1 for lattice occupied by monomer A, 2 for lattice occupied by monomer B and 3 for lattice occupied by the first fixed monomer X, respectively. Three one-dimensional arrays record the site of monomers in the linear chain, x, y and z , respectively. The first monomer of the chain is fixed on the flat surface $(0, 0, 1)$, marked the element of three-dimensional array $g[x[i]][y[i]][z[i]]$ with $i = 0$ for the first monomer X of the chain. The coordinate of the first monomer of the chain is fixed as follows:

```

i = 0
x[i] = 0;
y[i] = 0;
z[i] = 1;
g[x[i]][y[i]][z[i]] = 3;

```

The new monomer from 1 to N is generated by self-avoiding walk at random.

```

for (i = 1; i <  $N$ ; i + +) {
    do {
        k = (int) 6 * rand(); // a random number selected one of six motion directions
        x[i] = x[i-1] + dx[k];
        y[i] = y[i-1] + dy[k];
    }
}

```

```

z[i]= z[i-1] + dz[k];
} while (g[x[i]][y[i]][z[i]]) == 0 && z[i]> 0);

//set the state of the monomer i in space 1-A, 2-B
if (i<N/2)
    g[x[i]][y[i]][z[i]]= 1;
else
    g[x[i]][y[i]][z[i]] = 2;

}

```

At the beginning of simulation, a SAW polymer chain is to generate at first. The number of monomer A and the number of monomer B in the diblock copolymer are both equal to $N/2$ half of the chain length. In this simulation, there are two sequences of diblock copolymer by which segment is grafted onto the monomer X: $XA_{N/2}B_{N/2}$ for the end of segment A grafted onto the monomer X and $XB_{N/2}A_{N/2}$ for the end of segment B grafted onto X.

2.2 Chain Motion Method

After generating a whole chain, the chain maintain Brownian motion constantly. In the motion model, one monomer is chosen randomly and attempts to move one step selected randomly from one of the six directions. The motion of the polymer chain is simulated by the bond fluctuation model. The bond length in three dimensional lattice model is allowed as three conditions: 1, $\sqrt{2}$ and $\sqrt{3}$. In our bond fluctuations model, each site of the lattice has the coordination number $z=26$ in three-dimensional space, and $z=8$ in two-dimensional space. Each monomer contacting to the surface has an interaction energy E . Each monomer of chain except the first one is always doing Brownian motion. In the simulation, the monomer is selected randomly from 1 to N and the direction is also selected randomly. One attempt to move is to meet the following conditions:

(1) One of monomers, which is selected random from 1 to N in chain, try to move one step.

$$i = (\text{int}) (N * \text{rand} ()+1); \quad (1)$$

(2) Check the nearest neighbor (NN) lattice of *monomer i* along the six directions. If the NN lattice is empty, the sequence number of the direction will be recorded. And a number randomly selected from these allowed directions is assigned to motion direction k .

(3) The new position of *monomer i* is located above the surface ($z[i]+dz[k] > 0$).

(4) The new bond length between *monomer i* and the nearest neighbor monomer $i-1$ or $i+1$ meet the allowed conditions (1, $\sqrt{2}$, $\sqrt{3}$).

(5) This monomer i can move with probability $\exp(-\Delta E/k_B T)$ which is the Boltzmann factor, where ΔE is the energy migration before and after the motion. The Boltzmann constant k_B is set unity in the simulation.

If all the conditions (1) - (5) are met, *monomer i* moves successfully one step. When all monomers attempt to exercise once, the time is recorded as a Monte Carlo Step (MCS).

2.3 Parallel Computing Method.

Static and dynamic properties of the polymer chain are simulated by the parallel computing method. A large number of samples are calculated for sampling statistics. At each sample, the chain is produced independently by self-avoid walk and then the polymer chain has been doing Brownian motion. The thermodynamic and kinetic properties of the polymer are calculated and recorded at different temperatures. At each temperature T , the polymer chain first run enough relaxation time for about $2.5N^{2.13}$ MCS [15-16]. And then chain continue to do Brownian motion in the next $100 N^{2.13}$ MCS, in which we record chain properties at every $0.1N^{2.13}$ MCS. Over 1000 conformations are averaged for one independent sample. We calculate 1000 independent samples for statistic average. And the final results are averaged over 10^6 independent conformations. These individual samples are run by parallel computing in the cluster of the high-performance computing center.

The parallel algorithm is to implement through Fortran+MPI (Message Passing Interface) and the program flowchart is described in Figure 1.

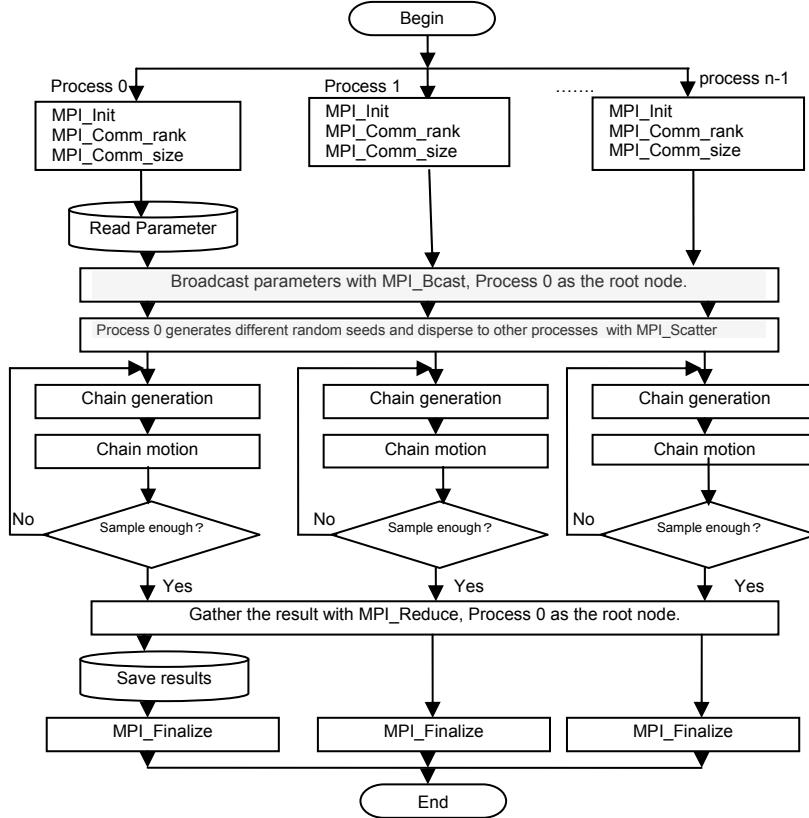


Figure 1. Parallel Program Network Charts

3. Results and Analysis

In this section, it is explained the results of Monte Carlo simulation and at the same time is given the comprehensive discussion. The critical adsorption point (CAP) could be understood as the point where the limiting monomer free energy for a chain attached to the surface equals the limiting monomer free energy of a desorbed chain in the bulk solution [15]. The statistical approach is always to study the conformation of polymers. Probabilities of the different conformations produces a polymer chain with many possible shapes [17]. Finally, the speedup of our parallel computing is discussed.

3.1. Adsorption Properties

The analysis of the number of surface contacts M is always to determine the critical adsorption point (CAP) of polymers. We calculated the mean number of surface contacts $\langle M \rangle$ of diblock copolymer chain $X_{N/2}B_{N/2}$, $XB_{N/2}A_{N/2}$ and homopolymer chain $XA_{N/2}$ with chain length $N=400$ at different temperatures in Figure 2. At low temperatures, $\langle M \rangle$ of these three polymers are almost the same value at the same temperature. Near the critical adsorption point, the mean surface contacts $\langle M \rangle$ of homopolymer $XA_{N/2}$ is the biggest, $\langle M \rangle$ of $XB_{N/2}A_{N/2}$ is the smallest, and $\langle M \rangle$ of $X_{N/2}B_{N/2}$ is between them, as shown in the inset of Figure 2. This shows that the surface contacts $\langle M \rangle$ is affected by the segment B, which have none attractive at the surface, in front of or behind the segment A.

The mean number of surface contacts $\langle M \rangle$ of diblock copolymer $X_{N/2}B_{N/2}$ and $XB_{N/2}A_{N/2}$ is calculated for chain length $N=50, 100, 200$ and 400 at different temperature in Figure 3. At low temperature, $\langle M \rangle$ almost linearly increase as the temperature T decreases. At high temperature, $\langle M \rangle$ is almost 0 and does not change with the temperature T . $\langle M \rangle$ has a transition phase at about $T_c = 1.5$ for both diblock copolymer $X_{N/2}B_{N/2}$ and $XB_{N/2}A_{N/2}$.

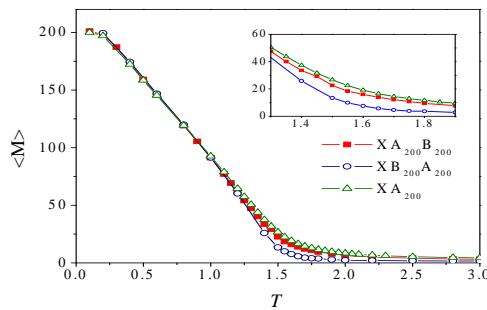


Figure 2. The Mean Number of Surface Contacts $\langle M \rangle$ at Different Temperatures for Diblock Copolymer Compared with Homopolymer.

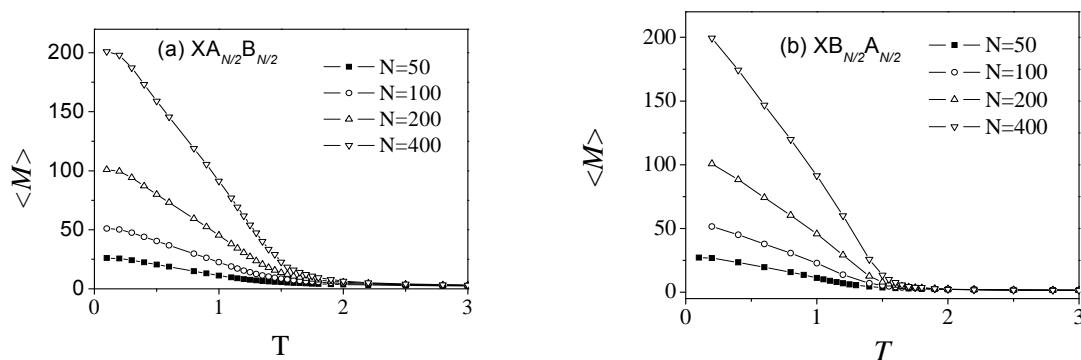


Figure 3. The dependence of the Mean Number of Surface Contacts $\langle M \rangle$ of Diblock Copolymer on Different Temperatures T for Chain Length $N=50, 100, 200$, and 400 . (a) $XA_{N/2}B_{N/2}$ and (b) $XB_{N/2}A_{N/2}$

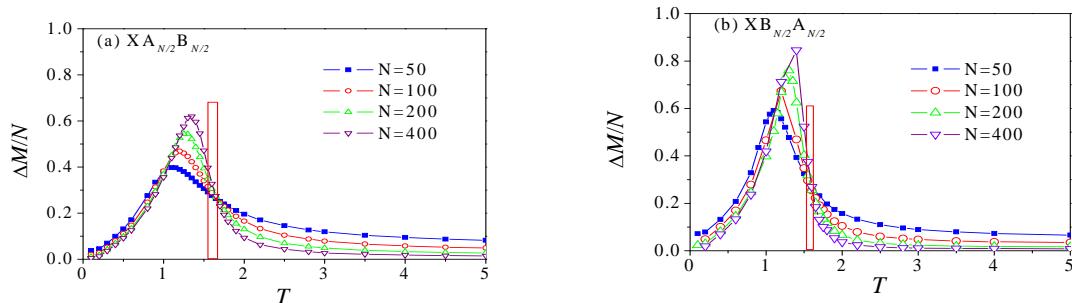


Figure 4. The Variance of the Order Parameter ΔM as a Function of Temperature T for Different Chain Length $N=50, 100, 200$ and 400 . (a) $XA_{N/2}B_{N/2}$ and (b) $XB_{N/2}A_{N/2}$

In simulations, we calculate the variance of the surface contacts, $\Delta M = \langle M^2 \rangle - \langle M \rangle^2$, where $\langle M^2 \rangle$ is the mean square number of adsorbed monomers and $\langle M \rangle$ is the mean number of adsorbed monomers. The variance of the surface contacts will produce some important thermodynamic quantities like specific heat by the fluctuation relations. The variance of the surface contacts ΔM exists a maximum at the temperature below and more close to the CAP with the increase of chain length N . The dependence of $\Delta M/N$ on the temperature T is plotted in Figure 4 for a variety of chain lengths N from 50 to 400. We find each curve for different length N nearly intersect at a common point, which is in excellent agreement with T_c of homopolymer

by scaling from $\langle M \rangle$ [11]. The variance of the surface contacts $\Delta M/N$ can be used to determine the CAP by the common intersection point of $\Delta M/N$ vs T . In the simulation we found that the intersection point for diblock copolymer is also in agreement with the CAP. The CAP of diblock copolymer is roughly equal to CAP of homopolymer. The critical adsorption point has none effect by segment B.

3.2. Conformation Properties

The shape of polymer can be described using the mean asphericity parameter $\langle A \rangle$ which is defined in three-dimension space as:

$$\langle A \rangle = \left\langle \sum_{i>j}^3 (L_i^2 - L_j^2)^2 / 2 \left(\sum_{i=1}^3 L_i^2 \right)^2 \right\rangle . \quad (2)$$

Here, L_1^2 , L_2^2 , and L_3^2 ($L_1^2 \leq L_2^2 \leq L_3^2$) are the eigenvalues of the radius of gyration tensor [17].

$$S = \frac{1}{n} \sum_{i=1}^n s_i s_i^T = \begin{pmatrix} S_{xx} & S_{xy} & S_{xz} \\ S_{xy} & S_{yy} & S_{yz} \\ S_{xz} & S_{yz} & S_{zz} \end{pmatrix}$$

Where $s_i = \text{col}(x_i, y_i, z_i)$ is the position of monomer i in a frame of reference with its origin at the center of mass. $\langle A \rangle$ ranges from 0 for spherically symmetric chain, to 0.5 for circular ones, and to 1 for rod-shaped ones. For a linear SAW chain, $\langle A \rangle$ is about 0.44 for long chain [11, 17].

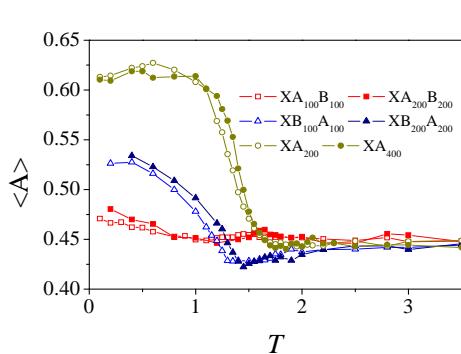


Figure 5. Plot of the Asphericity Parameter $\langle A \rangle$ Versus Temperature T for Chain Length $N = 200$ and 400

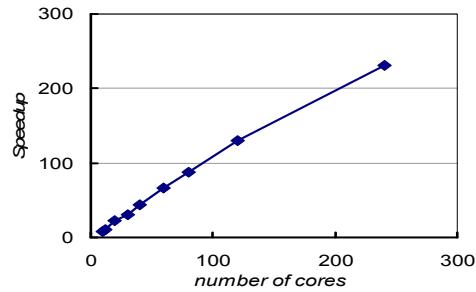


Figure 6. Plot of Speedup Versus the Number of Cores

We have calculated the mean asphericity parameter $\langle A \rangle$. Figure 5 shows the dependence of the mean asphericity parameter $\langle A \rangle$ on temperature T for diblock copolymer and compared with homopolymer, among which there is a great difference. For homopolymer, $\langle A \rangle$ exists a transition phase at T_c , at high temperature $\langle A \rangle = 0.45$ and at low temperature $\langle A \rangle = 0.62$. For the diblock copolymer $XA_{N/2}B_{N/2}$, $\langle A \rangle$ almost does not change, because segment B in the tail of copolymer extends freely in solution. For $XB_{N/2}A_{N/2}$, $\langle A \rangle$ almost remains unchanged at high temperature $T > T_c$, at low temperature $T < T_c$, $\langle A \rangle$ of $XB_{N/2}A_{N/2}$ increases as the temperature decreases, which is smaller than that of the homopolymer at the same temperature, since both ends of segment B close to the surface, but the middle of the monomers B can stretch in the solution. From the value of the shape factor at different temperatures, we can distinguish the polymer type.

3.3. Speedup

Numerical simulation of the self-avoiding chain is computed at high-performance server cluster. In order to test the speedup for the same chain length in different core number, the parameters are used for the chain length $N = 100$, the number of samples 480, Monte Carlo step 10^6 MCS. Speedup is dependent on the number of processor cores in the same parameters as shown in Figure 6. The test result is nearly linear speedup.

4. Conclusion

In this paper, Monte Carlo method is to study the adsorption and conformational properties of the polymer chain. The simulation is performed in parallel on a cluster. The simulation results indicate that there is a difference in the surface contacts for two different diblock copolymer chain, but the critical adsorption point is almost the same as CAP of the homopolymer chain. The conformational properties differences for diblock copolymers and homopolymer. We calculated the speedup of parallel computing, which is almost linear speedup.

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References

- [1] Asanovic K, Bodik R, Demmel J, Keaveny T. A View of the Parallel Computing Landscape. *Communications of the ACM*. 2009; 52(10): 56-67.
- [2] Asanovic K, Bodik R, Catanzaro BC. The Landscape of Parallel Computing Research:A View from Berkeley, tech. report UCB/EECS-2006-183. Dept. Electrical Eng. and Computer Science, Univ.of Calif., Berkeley. 2006.
- [3] Rauber T, Rungger G. Parallel Programming For Multicore and Cluster Systems. Springer-Verlag Berlin Heidelberg. 2010.
- [4] Bergeron B. Bioinformatics Computing, Prentice Hall PTR. 2002.
- [5] Li KB. ClustalW-MPI: ClustalW analysis using Distributed and Parallel Computing. *Bioinformatics*. 2003; 19(12): 1585-1586.
- [6] Gao HB, Li H. Computer Simulation for a Catalytic Reaction on Fractal Surfaces by Monte Carlo Method. *Recent Advances in CSIE LNEE*. 2011; 125: 647-652.
- [7] Besra L, Sengupta DK, Roy SK, Ay P. Influence of polymer adsorption and conformation on flocculation and dewatering of kaolin suspension. *Separation and Purification Technology*. 2004; 37: 231-246.
- [8] Gao HB. Computer Simulation of a Flexible Polymer Chain in a Slit. *Communications in Computer and Information Science*. ICHCC 2011, CCIS 163. 2011; 163: 417-424.
- [9] Li H, Qian CJ, Luo MB. Conformational properties of a polymer tethered to an interacting flat surface. *Polymer Journal*. 2010; 42:383.
- [10] De Gennes PG. Conformations of Polymers Attached to an Interface. 1980; 13: 1069-1075.
- [11] Li H, Qian CJ, Sun LZ, Luo MB. Simulation of a flexible polymer tethered to a flat adsorbing surface, *Journal Applied Polymer Science*. 2012; 124:282.
- [12] Gao HB, Li H, Qian CJ. Parallel Monte Carlo Simulation of Single Polymer Chain. *Applied Mechanics and Materials*. 2013; 263-266: 3317-3320.
- [13] Forrest BM, Baumgartner A, Heermann DW. Parallel Simulation of Dense Two-Dimensional Polymer Systems. 1990; 59: 455-462.
- [14] Uhlherr A. Parallel Monte Carlo Simulations by Asynchronous Domain Decomposition. *Computer Physics Communications*. 2003; 155: 31-41.
- [15] Luo MB. The critical adsorption point of self-avoiding walks: A finite-size scaling approach. *Journal Chem. Phys.* 2008; 128: 044912.
- [16] Luo MB, Huang JH. Monte Carlo simulation of polymer chain with ferromagnetic Ising interaction. *Journal. Chem. Phys.* 2003; 119: 2439.
- [17] Luo MB, Huang JH, Chen YC, Xu JM. Correlation between shape and size of linear polymer chains. *Eur. Polym. Journal*. 2001; 37: 1587.