Monte Carlo Study on Polymer Chain with One End Attached to a Surface

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Abstract The end-to-end vector distribution $P(\boldsymbol{R})$ of a linear random-flight polymer chain with one end attached to an infinite large flat surface is investigated by Monte Carlo method. The mean-square end-to-end distance can be given by $<R^2> = (4/3)n$, and the mean angle by $<\theta> = 45°$, where n is the chain length, θ is the angle between the end-to-end vector $\boldsymbol{R}$ and Z axis normal to the surface. The radial distribution is $P(R)\mathrm{d}R = 2A^4 \exp(-A^2R^2)R^3\,\mathrm{d}R$ and the angular distribution is $P(\theta)\mathrm{d}\theta = \sin 2\theta \mathrm{d}\theta$, here $A^2 = 3/(2n)$. The shape factor $<L_1^2>:<L_2^2>:<L_3^2>$ is about 1: 2. 73: 12. 5. The distribution of angle α, the angle between the longest principal axis L_3 and Z axis, is approximately $P(\alpha)\mathrm{d}\alpha = \sin\alpha d\alpha$, and its mean value $<\alpha>$ is nearly equal to 55. 5°.

Keywords: End-to-end vector, Shape factor, Distribution function, Polymer Chain

1 Introduction

Many important conformational properties of a flexible polymer chain can be characterized by the end-to-end vector distribution $P(\boldsymbol{R})$. The mean-square end-to-end distance $<R^2>$ can be calculated by

$$<R^2> = \int R^2 P(\boldsymbol{R})\mathrm{d}\boldsymbol{R} \qquad (1)$$

where R is the distance of $\boldsymbol{R}$. For free polymer chains, $P(\boldsymbol{R})$ is independent of angular variables since the polymer chains have spherical symmetry, i. e., $P(\boldsymbol{R}) = P(R)$. It is well known that $P(R)$ has a Gaussian form for long random-flight (RF) chains [1, 2].

The behavior of a polymer chain, confined to a restricted spatial region, is of importance for many practical problems, such as the adsorption of polymer, the stabilization of colloidal dispersion, and the gel permeation chromatography. Casassa [3, 4] investigated the density distribution of RF linear and star-branched polymer chains near a barrier using probability theory and Monte Carlo (MC) method. Shiokawa [5] studied $P(R)$ of a polymer chain with the excluded volume confined between two plates using the homotopy parameter expansion method, and found a vast difference between the distribution $P(R)$ of the confined chain and the Gaussian form.

Polymer chain with one end attached to a surface by means of physical or chemical interaction is an example of confined ones and has become one of the important subjects in polymer science [6]. Some configurations diminish when polymer chains are attached to a surface, giving rise to a number of interesting properties. Alexander and de Gennes[7-9] showed that the properties of end attached linear chains depend on the grafting density (chain number attached to per unit area): at low grafting density, the chains are independent of each other and form individual "mushrooms"; while at enough high grafting density, they stretch out to form "brushes".

Meanwhile, many efforts were devoted to study the shape of polymer chain [10-13]. And recently, it has been found that the shape of chain would influence the

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property of solid/liquid or oil/water interface [14] and stabilization of colloidal system [15]. In this work, the distribution function of end-to-end vector $P(\boldsymbol{R})$ and the shape of a linear RF chain with one end attached to an infinite large flat surface at very low grafting density was studied. Therefore, single polymer chain is introduced in the simulation space. We investigated the influence of the surface to the end-to-end vector distribution $P(\boldsymbol{R})$ and to the shape. Considering that the spherical symmetry was broken by the surface, we then investigated the distribution $P(\boldsymbol{R})$ by calculating its radial distribution $P(R)$ and angular distribution $P(\theta)$, where θ is the angle between end-to-end vector $\boldsymbol{R}$ and the direction Z normal to the surface.

2 Model and formulation

Consider a RF chain with $n+1$ segments (chain length n) serially numbered from 0 to n. Assuming an impermeable, noninteracting plane at $z=0$ of an orthogonal coordinate system (x, y, z), we can write the probability density $P_n(z, z_0)$ of finding the last segment (numbered n) at z with the first segment (numbered 0) fixed at $z_0 \geqslant 0$ as [16].

$$P_n(z,z_0) = \frac{A}{\sqrt{\pi}\, erf(Az_0)}\{\exp[-A^2(z-z_0)^2] - \exp[-A^2(z+z_0)^2]\} \quad (2)$$

Here $A^2 = 3/(2nb^2)$ and $erf(x)$ denotes error function which is defined as $erf(x) = \frac{2}{\sqrt{\pi}}\int_0^x \exp(-u^2)\mathrm{d}u$. The mean-square bond length b^2 is set to be 1 hereafter. While in x or y direction, the distribution still has a Gaussian form

$$P_n(x,x_0) = \frac{A}{\sqrt{\pi}}\exp[-A^2(x-x_0)^2] \quad (3)$$

For end attached RF chain ($z_0=0$), we get the end-to-end vector distribution $P(\boldsymbol{R})$ in a spherical coordinate system (R, θ, ϕ)

$$P(\boldsymbol{R})\mathrm{d}\boldsymbol{R} = P(R,\theta)2\pi R^2\sin\theta \mathrm{d}R\mathrm{d}\theta = 2A^4\exp(-A^2R^2)R^3\mathrm{d}R\sin 2\theta \mathrm{d}\theta \quad (4)$$

with the end-to-end distance $R\in(0,\infty)$ and the angle $\theta\in(0,\pi/2)$.

Thus the radial distribution $P(R)$ and the angular distribution $P(\theta)$ of the end grafted chain are

$$P(R)\mathrm{d}R = 2A^4\exp(-A^2R^2)R^3\mathrm{d}R \quad (5.1)$$

and

$$P(\theta)\mathrm{d}\theta = \sin 2\theta \mathrm{d}\theta \quad (5.2)$$

respectively. Eq. 5. 1 implicitly indicates that, comparing with the Gaussian distribution, the probability of large R increases while that of small R decreases. From Eqs. 5. 1 and 5. 2, one could easily deduce the mean-square end-to-end distance $\langle R^2\rangle = (4/3)n$ and mean angle $\langle\theta\rangle = \pi/4$ (or 45°), respectively.

The end-to-end vector distribution of end attached RF chain was also investigated using MC method. In this method, the chain is constructed by adding segments one-by-one. The bond length is fixed to 1. The first segment is put at (0, 0, 0). Each segment is randomly located on a spherical surface of unit radius with its center at the previous segment, with a construction probability proportional to the portion of the area of spherical surface in the upper half space. Therefore, the construction probability of the second segment (numbered 1) $p_1 = 1/2$, and that of the segment i (numbered i) is

$$p_i = \begin{cases} 1, & z_{i-1}\geqslant 1 \\ \frac{1+z_i}{2}, & z_{i-1} < 1 \end{cases} \quad (6)$$

where z_i is the z coordinate of segment i. Therefore, the construction probability of a whole chain is

$$P_{\text{chain}} = \prod_{i=1}^{n} p_i.$$

After a polymer chain of length n is successfully generated, the radius of gyration tensor S is calculated as

$$S = \frac{1}{n+1}\sum_{i=0}^{n} s_i\cdot s_i^{\mathrm{T}} = \begin{pmatrix} S_{xx} & S_{xy} & S_{xz} \\ S_{xy} & S_{yy} & S_{yz} \\ S_{xz} & S_{yz} & S_{zz}\end{pmatrix} \quad (7)$$

Here, $s_i = \mathrm{col}(x_i, y_i, z_i)$ is the position vector of segment i in a frame of reference with its origin at the center of mass. S is a symmetric matrix and can be diagonalized with three eigenvalues L_1^2, L_2^2 and L_3^2 ($L_1 \leqslant L_2 \leqslant L_3$) and three corresponding eigenvectors

$\vec{q}_1$, $\vec{q}_2$ and $\vec{q}_3$, respectively. The angle α between the longest principal axis L_3 and z axis ($0 \leqslant \alpha \leqslant \pi/2$) is calculated as

$$\alpha = \cos^{-1} |\vec{q}_3 \cdot \vec{e}_z| \tag{8}$$

here $\vec{e}_z$ is the unit vector of the direction z.

The number of samples (individual chains) required for calculating the statistical averages is 10^6, while that for distribution is 10^7. The weight of each sample for averaging is its construction probability P_{chain}. The chain lengths n considered are from 10, 20, up to 1000.

3 Results

In Fig. 1 shows the MC result of the distribution $P(R)$ for end attached RF chain of length $n = 1000$. It can be seen that the MC result is in good agreement with Eq. 5.1. The mean-square end-to-end distance $<R^2>$ of end attached chain is linearly proportional to chain length n (see inset in Fig. 1),

$$<R^2> \approx 1.32\ n \tag{9}$$

which is in good agreement with the theoretical prediction. The $<R^2>$ of the corresponding free RF chain is $<R^2> \approx n$, indicating that the flat surface plays a repulsive effect on the polymer chain. As a view from the probability distribution $P(R)$, one finds that the probability of large R increases for end attached chain.

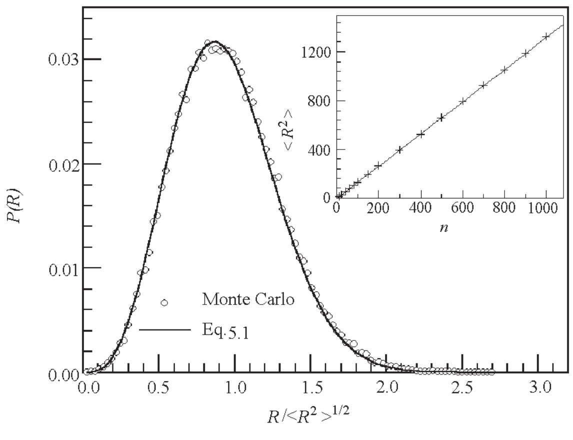

Fig. 1 The radial distribution $P(R)$ of end grafted polymer chain *vs* the scaled end-to-end distance $R/<R^2>^{1/2}$

Inset: Plot of the mean-square end-to-end distance $<R^2>$ *vs* the chain length n. Symbols (+) are the MC results, and the solid line is the linear fit

The repulsive effect of the surface keeps the segments of chain away from the surface, which causes $<R^2>$ larger. For this reason, one could expect that it will also reduce the angle $<\theta>$. It is well known that, if one introduces an arbitrary axis, the mean angle $<\theta>$ of the free chain is 57.3°. As expected, the MC result of $<\theta>$ is smaller than 57.3°. The mean angle $<\theta>$ and the angular distribution $P(\theta)$ are both consistent with the theoretical prediction of Eq. 5.2 (also see Fig. 2 and 3), and the difference between MC calculation and the theoretical value is very small. Moreover, the decrease of $<\theta>$ with chain length indicates that the repulsive effect on a long chain is more evident than that

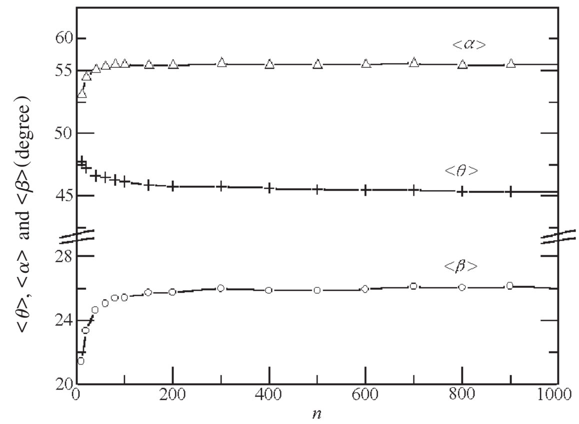

Fig. 2 Plot of the mean angles $<\theta>$, $<\alpha>$ and $<\beta>$ of end attached polymer chain *vs* the chain length n

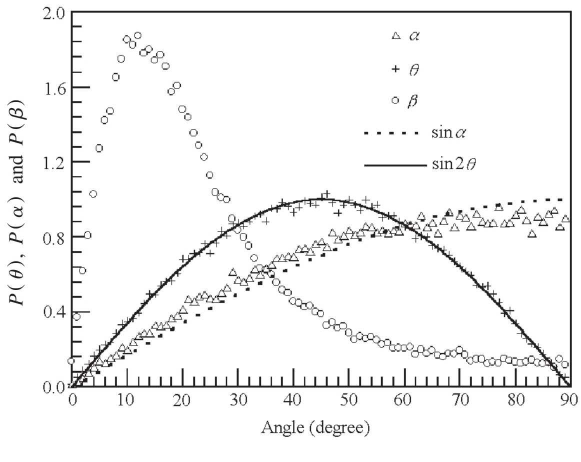

Fig. 3 The angular distributions $P(\theta)$, $P(\alpha)$ and $P(\beta)$ of end attached polymer chain *vs* the angles for chain length $n = 1000$

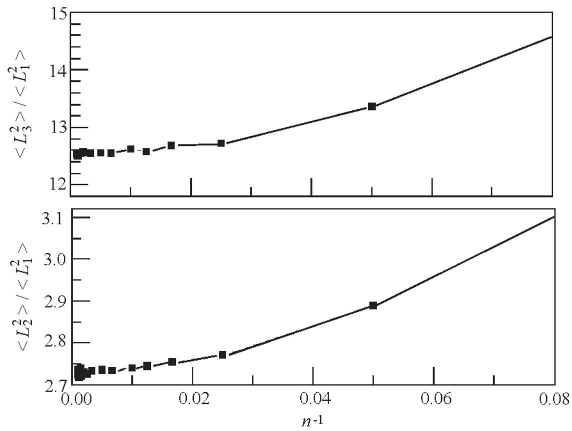

Fig. 4 The dependence of shape factors of end attached polymer chain on the reciprocal of chain length n^{-1}

on a short one. Since $P(\theta=90°)=0$ for end-grafted chain, one will find that only a small fraction of segments is near the surface.

Fig. 4 shows the dependence of shape factors, $<L_2^2>/<L_2^1>$ and $<L_2^3>/<L_2^1>$, on the reciprocal of chain length n^{-1} for end attached RF chain. The asymptotic values of shape factor $<L_1^2>:<L_2^2>:<L_3^2>$ is about 1: 2. 73: 12. 5, larger than that of the free chain, $<L_2^1>:<L_2^2>:<L_3^2>\approx 1:2.7:11.8$ [10]. Therefore, one could see that the end attached chains are much more elongated. Our simulation of shape factors of end attached RF chain is in good agreement with that of lattices model[17].

The surface not only influences the shape of the chain, but also affects the chain orientation. This can be found from the mean value of angle $<\alpha>$, α being the angle between the longest principal axis L_3 and z axis, and the distribution $P(\alpha)$. As is well known, in the absence of any restriction to the chain, $<\alpha>$ could be 57. 3° and $P(\alpha)$ be a sine distribution, i. e., $P(\alpha)\mathrm{d}\alpha=\sin\alpha\mathrm{d}\alpha$. However, we find in the constrained case a slight deviation of the distribution $P(\alpha)$ from $\sin\alpha$, and $<\alpha>$ is about 55. 5°, slightly smaller than 57. 3°.

The drop of $<\alpha>$ comes from the orientational correlation between the largest principal axis L_3 and end-to-end vector $\boldsymbol{R}$. Since the mean-square distance between the segments i and j of a RF chain is roughly given by $R_{ij}^2\propto|j-i|$, the root-mean-square end-to-end distance is on average the longest distance between any two segments. This suggests a certain correlation between the direction of end-to-end vector and that of the longest principal axis. Supposing no correlation exists, the mean value of angle β included between the direction of end-to-end vector and that of the longest principal axis would be 57. 3° and the distribution of β be a sine distribution. However, simulation results show that $<\beta>$ is about 27° and $P(\beta)$ shows large deviation from the sine distribution. Therefore, our simulation really indicates that there exists the orientational correlation between L_3 and $\boldsymbol{R}$ for end-grafted chain. Since the surface imposes a repulsive effect on $\boldsymbol{R}$, the angle θ decreases, therefore it's reasonable that angle α also decreases. Moreover, we found a peak in $P(\beta)$ near $\beta=10°$.

4 Conclusions

The end-to-end vector distribution $P(\boldsymbol{R})$ of the linear polymer chain with one end attached to a plat surface was investigated. We found that the mean-square end-to-end distance $<R^2>=(4/3)n$, and the mean angle $<\theta>=45°$. The radial distribution $P(R)\mathrm{d}R=2A^4\exp(-A^2R^2)R^3\mathrm{d}R$ and the angular distribution $P(\theta)\mathrm{d}\theta=\sin2\theta\mathrm{d}\theta$. The shape factor $<L_1^2>:<L_2^2>:<L_3^2>$ of end-grafted chain is about 1: 2. 73: 12. 5, larger than that of a free chain. The distribution of angle α is approximately $P(\alpha)\mathrm{d}\alpha=\sin\alpha\mathrm{d}\alpha$, and its mean value $<\alpha>$ is nearly equal to 55. 5°. Results also showed the orientational correlation between the largest principal axis L_3 and end-to-end vector $\boldsymbol{R}$. The mean value of β is about 27° and a peak in $P(\beta)$ is near $\beta=10°$. These results can be used as a guidance for some more complicated cases, such as chain with excluded volume, real polymer chain, etc.

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端基被平面壁吸附的高分子链的 Monte Carlo 研究

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摘要 运用 Monte Carlo 方法研究了端基被无限大平面壁吸附的线型无规飞行链的末端距矢量 $\boldsymbol{R}$ 的分布 $P(\boldsymbol{R})$和链的形状,计算了末端距矢量 $\boldsymbol{R}$ 与 z 轴(垂直于平板)的夹角 θ,链的最大主轴 L_3 与 z 轴的夹角 α,以及 $\boldsymbol{R}$ 与 L_3 的夹角 β 的平均值$<\theta>$、$<\alpha>$、$<\beta>$和各自的分布 . 得到如下结论:

1. 端基吸附的高分子链的均方末端距$<R^2>\approx(4/3)n$,末端距矢量的径向分布为非高斯型,$P(R)\mathrm{d}R=2A^4\exp(-A^2R^2)R^3\mathrm{d}R$,其中 n 为链长,$A^2=3/(2n)$. 表明链受到限制后,较小的末端距 R 的分布概率减小,而较大的 R 的分布概率增大,导致链变得较为伸展 .

2. 角 θ 的平均值$<\theta>\approx 45°$,分布为 $P(\theta)\mathrm{d}\theta=\sin 2\theta\mathrm{d}\theta$,表明吸附高分子链的末端极少处于平面附近,即平面对高分子链具有排斥作用 . 但角 α 的平均值$<\alpha>\approx 55.5°$,分布近似为 $P(\alpha)\mathrm{d}\alpha=\sin\alpha\mathrm{d}\alpha$,均与自由链的情况相近,表明平面对最大主轴 L_3 的方向的影响不大 .

3. 端基吸附的高分子链的末端距矢量 $\boldsymbol{R}$ 与最大主轴 L_3 之间有较强的关联,它们的夹角 β 的平均值$<\beta>\approx 27°$,其分布的峰值所对应的 β 值约为 10°.

4. 吸附高分子链的形状更偏离球形,形状因子$<L_1^2>:<L_2^2>:<L_3^2>$约等于 1:2.73:12.5.

关键词: 末端距矢量, 形状因子, 分布函数, 高分子链

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