

THE PROPERTIES OF A SINGLE POLYMER CHAIN IN SOLVENT CONFINED IN A SLIT: A MOLECULAR DYNAMICS SIMULATION*

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Abstract A single polymer chain in solvent confined in a slit formed by two parallel plates is studied by using molecular dynamics simulation method. The square radii of gyration and diffusion behaviors of polymers are greatly affected by the distance between the two plates, but they do not follow the same way. The chain size decays drastically with increasing h (h is the distance between two plates), until a basin occurs, and a universal $h/\langle R_g \rangle_0$ dependence for polymer chains with different degrees of polymerization can be obtained. While, for the chain's diffusion coefficient, it decays monotonously and there is no such basin-like behavior. Furthermore, we studied the radial distribution function of confined polymer chains to explain the reason why there is a difference for the decay behaviors between dynamic properties and static properties. Besides, we also give the degree of confinement dependence of the static scaling exponent for a single polymer chain. Our work provides an efficient way to estimate the dynamics and static properties of confined polymer chains, and also helps us to understand the behavior of polymer chains under confinement.

Keywords: Radius of gyration; Diffusion coefficient; Confinement; Radial distribution function; Parallel plates.

INTRODUCTION

Studies on the properties of confined polymer chains in solution are of great importance for their application in size exclusive and hydrodynamic chromatography, capillary electrophoresis, corrosion protective coatings, drug reduction, biological microstructures, lubricants and adhesives systems^[1, 2], and will be helpful for designing macromolecular micro separators^[3–5]. Typical work in this area mainly includes one^[6, 7] or two^[8–10] dimensional confinement, especially for the static behavior of confined polymer systems^[11–28]. In last two decades, one-dimension confined polymer system has attracted a lot of attention^[17–26]. ten Brinke and van Vliet *et al.*^[20, 21] reported that a polymer chain between two parallel plates first oriented parallel to the plates and then it was squeezed with the decrease of the slit width. Romiszowski and Sikorski^[19, 29] found that the terminal parts of confined polymers were mostly exposed to the plates while their centers remained hidden away from the plates and verified the universal behavior of polymer size. Similar behaviors were also observed for star-branched polymers^[22] and biomolecules like DNA^[30–33]. However, these reports do not give the information about confinement effect on the dynamic behavior of polymers, which is necessary for polymers' widely application in commercial production.

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For a confined polymer chain, its dynamic property is supposed to be changed greatly by the confinement effect. Brochard and de Gennes^[34] studied the dynamic behaviors of a self-avoiding chain confined in a slit through a scaling analysis, and obtained the friction coefficient for a confined polymer chain. Their results are different from those obtained by Debye-Bueche approximation, which is qualitatively efficient for 3-dimensional solution. Milchev, Binder and Dimitrov *et al.*^[28, 35–38] studied the dynamic properties of polymer chains in very strongly limited systems and found the result in agreement with Rouse model of excluded volume in 2-dimensions. However, the hydrodynamic interactions mediated by the solvent were not considered in their work. In this work, we will focus on the dynamic properties of confined polymer chains in a slit with various degree of confinement, considering the hydrodynamic interactions in solution. Moreover, we want to give a direct description of the confinement effect on the dynamic properties of polymer chains, and then we will discuss the difference between dynamic and static properties of a single polymer chain in solvent under confinement. In this work, the properties of a single polymer chain in solvent confined in a slit are studied by using molecular dynamics (MD) simulation method, where the slit is formed by two parallel plates with a distance of h apart, as shown in Fig. 1. The h dependence of the molecular size, diffusion and the shape of single confined polymer chain are investigated, and a universal law for the h dependence of polymers' static and dynamic properties is obtained.

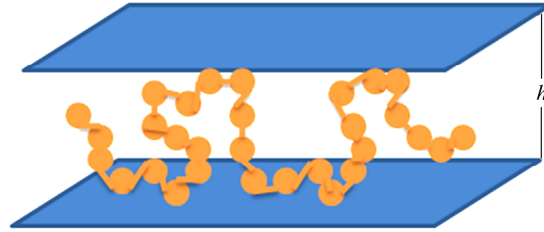


Fig. 1 The sketch of a single polymer chain confined in a slit formed by two parallel plates

MODEL AND SIMULATION DETAILS

The bead-spring model is employed to describe the polymer chain, and the solvent is taken to be athermal for the polymer chain. The shifted Lennard-Jones potential U_{LJ} and finitely extensible nonlinear elastic (FENE) potential U_{FENE} are used to embody excluded volume effect and the connection between neighboring monomers along chain bone^[39–41], respectively, *i.e.*

$$U_{LJ}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 + 1 \right] & r < r_c \\ 0 & r \geq r_c \end{cases} \quad (1)$$

and

$$U_{FENE}(r) = -\frac{k}{2} R_0^2 \ln \left(1 - \frac{r^2}{R_0^2} \right) \quad (2)$$

where, r is the distance between two interacting particles, and μ , σ , ϵ are respectively defined as the units of mass, length and energy. Subsequently, in reduced units, the cutoff diameter is set to be $r_c = 2^{1/6}\sigma$, the ultimate bond length^[42, 43] is $R_0 = 1.5\sigma$, the spring constant is $k = 30.0(\epsilon/\sigma^2)$, and time is in the unit of $\tau_{LJ} = (m\sigma^2/\epsilon)^{1/2}$ (1 time step = 0.006 τ_{LJ})^[40, 44].

The confinement is introduced by setting a single polymer chain in athermal solvent limited between two plates paralleling with xy plane at 0 and h positions in the z direction, where reflecting boundary condition is

employed^[7, 11, 39, 45]. We retain periodic boundary conditions in x, y directions and keep the total number of particles $N_{\text{tot}} \approx 8000$. For comparison, we also investigate the properties of an unconfined single chain in solvent by simulating the system in a simple cubic box (total volume $V = L \times L \times L$) of side length $L = 20.0\sigma$, in which periodic boundary condition are used in x, y , and z directions, and number density is $\rho = 1.0$ ($1/\sigma^3$). The value of h reflects the degree of confinement for a given polymer chain in solvent, namely, systems with small h have strong confinement and vice versa. In our simulation, the temperature is kept at $k_B T = 1.2\epsilon$ (k_B is Boltzmann constant) controlled by Berendsen method^[39, 46], and the motion equation of each particle is integrated by Leap-frog algorithm and accelerated by Verlet-cell list method^[39, 40]. After relaxing 6.0×10^6 time steps, the systems reach equilibrium. Then the data are collected every 200 time steps in the following 6.0×10^6 time steps^[40, 44]. Five parallel samples are measured to obtain better statistic results.

In this work, the molecular size, molecular shape, and diffusion behavior of the confined single polymer chain in solvent are studied. The molecular size is measured by the mean square radius of gyration $\langle R_g^2 \rangle$ defined as^[40, 47]

$$\langle R_g^2 \rangle = \frac{1}{2N^2} \sum_{m=1}^N \sum_{n=1}^N (\vec{r}_n - \vec{r}_m)^2 \quad (3)$$

herein, N is the degree of polymerization of the polymer chain, and $\vec{r}_m, \vec{r}_n$ are the position vectors of the m -th and n -th monomers, respectively. The molecular shape is characterized by a tensor $\mathbf{Q}$ describing the mass distribution of a polymer chain whose component is

$$Q_{\alpha\beta} = \frac{1}{N} \sum_{i=1}^N (r_{\alpha i} - \bar{r}_\alpha)(r_{\beta i} - \bar{r}_\beta) \quad (4)$$

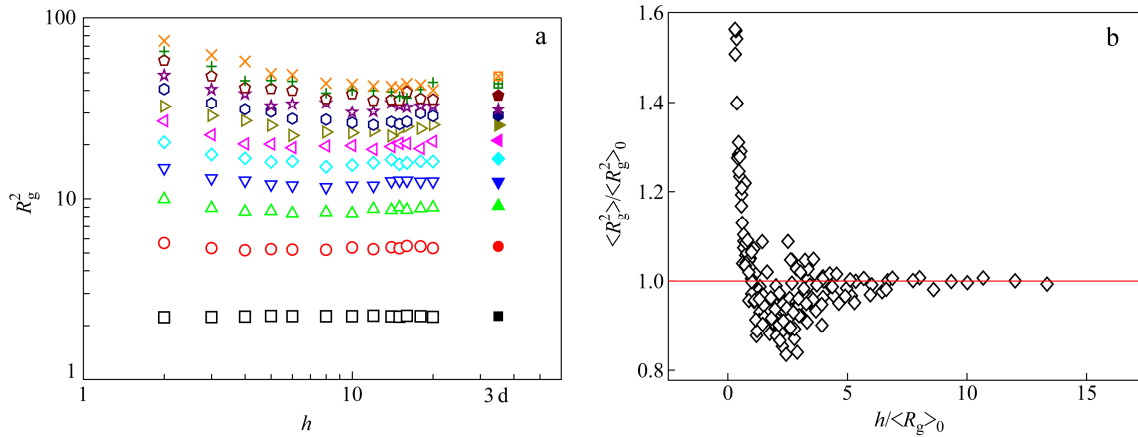
where $r_{\alpha i}, r_{\beta i}, \bar{r}_\alpha, \bar{r}_\beta$ are the α, β components of the position vector of the i -th monomer and the mass center of a polymer chain, respectively. Its three eigenvalues q_1, q_2, q_3 satisfy $q_1 > q_2 > q_3$ and $q_1 + q_2 + q_3 = \langle R_g^2 \rangle$, and the ratios among them present the molecular shape of a polymer chain^[41, 48].

RESULTS AND DISCUSSION

In this study, the degree of polymerization N of single polymer chains in solvent is changed from 10 to 120, and the distance between two plates h is varied from 2.0σ to 20.0σ . Therefore, the distance studied in this work is in the range of *ca.* $0.3\langle R_g \rangle_0$ to *ca.* $3\langle R_g \rangle_0$ for the longest polymer chain (*i.e.*, $N = 120$), and *ca.* $1.3\langle R_g \rangle_0$ to *ca.* $13\langle R_g \rangle_0$ for the shortest chain ($N = 10$), where $\langle R_g \rangle_0$ is the radius of gyration of polymer chain in three dimensions. We first concentrate on the mean square radius of gyration $\langle R_g^2 \rangle$ of a single polymer chain under confinement, and the results are listed in Table 1 and plotted in Fig. 2(a). For comparison, the properties of single polymer chain in solvent without confinement are also given in these tables and the following figures. It is seen that $\langle R_g^2 \rangle$ decays rapidly with the increase of h for all the studied polymer chains. The degree of confinement of a polymer chain imposed by the parallel plates is associated with the size of polymer chain, and therefore, we introduce a reduced distance, which is defined as $h/\langle R_g \rangle_0$, to study the effect of confinement on the properties of polymer. We also normalize $\langle R_g^2 \rangle$ of polymer chains under confinement with $\langle R_g^2 \rangle_0$ and plot them in Fig. 2(b). It is seen that an almost overlapping master curve for $\langle R_g^2 \rangle / \langle R_g^2 \rangle_0$ can be obtained, which means the decay of the size of confined polymer chains only depends on the relative degree of confinement (*i.e.* $h/\langle R_g \rangle_0$). Besides, with the increase of confinement, a basin^[19–21, 49–51] emerges when $h/\langle R_g \rangle_0 < 4.0$, and its minimum point is at about $h/\langle R_g \rangle_0 \approx 2.0$, being similar with the Doyle and Chen *et al.*'s results^[33, 51]. This basin suggests that when the polymer chain feels the confinement from the plates, it squeezes itself first before stretching, so that the size of confined polymer chains increases sharply when $h/\langle R_g \rangle_0$ is small enough.

Table 1. The h dependence of mean square radius of gyration $\langle R_g^2 \rangle$ of confined polymer chains (3d represents the data obtained in 3-dimensional unconfined systems.)

$h \backslash N$	10	20	30	40	50	60	70	80	90	100	110	120
2.0	2.2	5.7	10.0	14.8	20.6	27.0	32.6	40.7	48.3	58.3	65.6	74.7
3.0	2.2	5.3	8.9	13.0	17.6	22.6	28.9	33.9	40.4	47.8	54.2	62.6
4.0	2.2	5.2	8.5	12.6	16.8	20.1	27.2	31.5	38.2	41.2	45.2	57.8
5.0	2.2	5.2	8.6	12.1	16.0	20.1	25.6	30.5	32.8	40.8	45.2	49.4
6.0	2.2	5.2	8.3	11.9	16.1	19.2	22.5	27.8	33.6	39.8	44.8	48.7
8.0	2.2	5.2	8.4	11.6	15.1	19.6	23.4	27.5	34.1	35.9	38.7	43.7
10.0	2.2	5.4	8.3	11.9	15.4	19.7	23.2	26.4	30.1	38.1	40.0	43.2
12.0	2.3	5.2	8.8	11.9	15.8	18.8	23.9	25.7	30.5	35.0	39.9	42.2
14.0	2.2	5.4	8.7	12.6	16.5	19.4	22.3	26.8	34.1	35.4	39.3	41.9
15.0	2.2	5.3	9.0	12.6	15.6	20.3	24.2	26.0	32.7	35.1	37.1	41.4
16.0	2.3	5.5	8.7	12.6	15.8	20.3	25.2	26.8	32.2	39.1	36.4	43.6
18.0	2.2	5.4	8.9	12.5	16.1	19.0	24.5	29.8	32.8	35.9	40.5	42.9
20.0	2.2	5.3	9.0	12.5	16.1	20.8	25.7	28.8	32.8	35.5	44.3	40.2
3d	2.2	5.4	9.2	12.4	16.7	21.0	25.6	29.1	31.3	37.4	43.5	47.8

**Fig. 2** (a) The h dependence of the mean square radius of gyration $\langle R_g^2 \rangle$ of the single confined polymer chains with $N = 10$ ($\square$), 20 ($\circ$), 30 ($\triangle$), 40 (∇), 50 ($\diamond$), 60 ($\triangleleft$), 70 ($\triangleright$), 80 ($\odot$), 90 ($\star$), 100 ($\diamond$), 110 ($+$), 120 ($\times$) (The corresponding solid symbols and $\boxplus$, $\boxtimes$ represent the data obtained from 3-dimensional unconfined systems.); (b) The normalized $\langle R_g^2 \rangle / \langle R_g^2 \rangle_0$ of these confined polymer chains plotted as functions of $h / \langle R_g \rangle_0$

For a single polymer chain in confinement (the confinement is imposed in z -direction), the diffusion along z -direction will show a different way from that in other directions. Therefore, for the dynamic property of a confined polymer chain, we distinguish its diffusion behavior into two directions, which are parallel and vertical to the confining plates, respectively. Diffusion coefficient of a confined polymer chain along confining plates are characterized by the diffusion coefficient $D_{\text{cm},//}$ of the mass center of the polymer chain paralleling to the plates, which is defined as^[40, 52]

$$4D_{\text{cm},//}t = \left\langle \left(\bar{r}_{\text{cm},//}(t) - \bar{r}_{\text{cm},//}(0) \right)^2 \right\rangle \quad (5)$$

where $\bar{r}_{\text{cm},//}(t)$ is the position vector of the mass center for the polymer chain along confining plates at time t , and $\left\langle \left(\bar{r}_{\text{cm},//}(t) - \bar{r}_{\text{cm},//}(0) \right)^2 \right\rangle$ is the corresponding mean square displacement of the confined polymer chain. The diffusion behavior of a confined polymer chain vertical to the plates (z -direction) is directly described by its mean square displacement $\left\langle \left(\bar{r}_{\text{cm},z}(t) - \bar{r}_{\text{cm},z}(0) \right)^2 \right\rangle$ at z -direction. The $D_{\text{cm},//}$ values of confined polymer chains are

listed in Table 2 and plotted in Fig. 3, where $D_{\text{cm},0}$ represents the diffusion coefficient of a single polymer chain gained in a 3-dimensional unconfined system. The corresponding z -direction mean square displacements $\langle(\vec{r}_{\text{cm},z}(t) - \vec{r}_{\text{cm},z}(0))^2\rangle$ are given in Figs. 3(c)–3(f). For simplicity, we only illustrate four typical systems with $h = 2, 5, 8$ and 10 , respectively. With the increase of h , $D_{\text{cm},//}$ (Fig. 3a) of polymer chains first decays drastically, and then reaches a plateau when h is high enough. Furthermore, the decay behaviors of $D_{\text{cm},//}$ for polymer chains with different chain lengths are of great similarity, implying the confinement effect on the diffusion of polymer chains only depends on the slits interval h , which can also be seen from the mean square

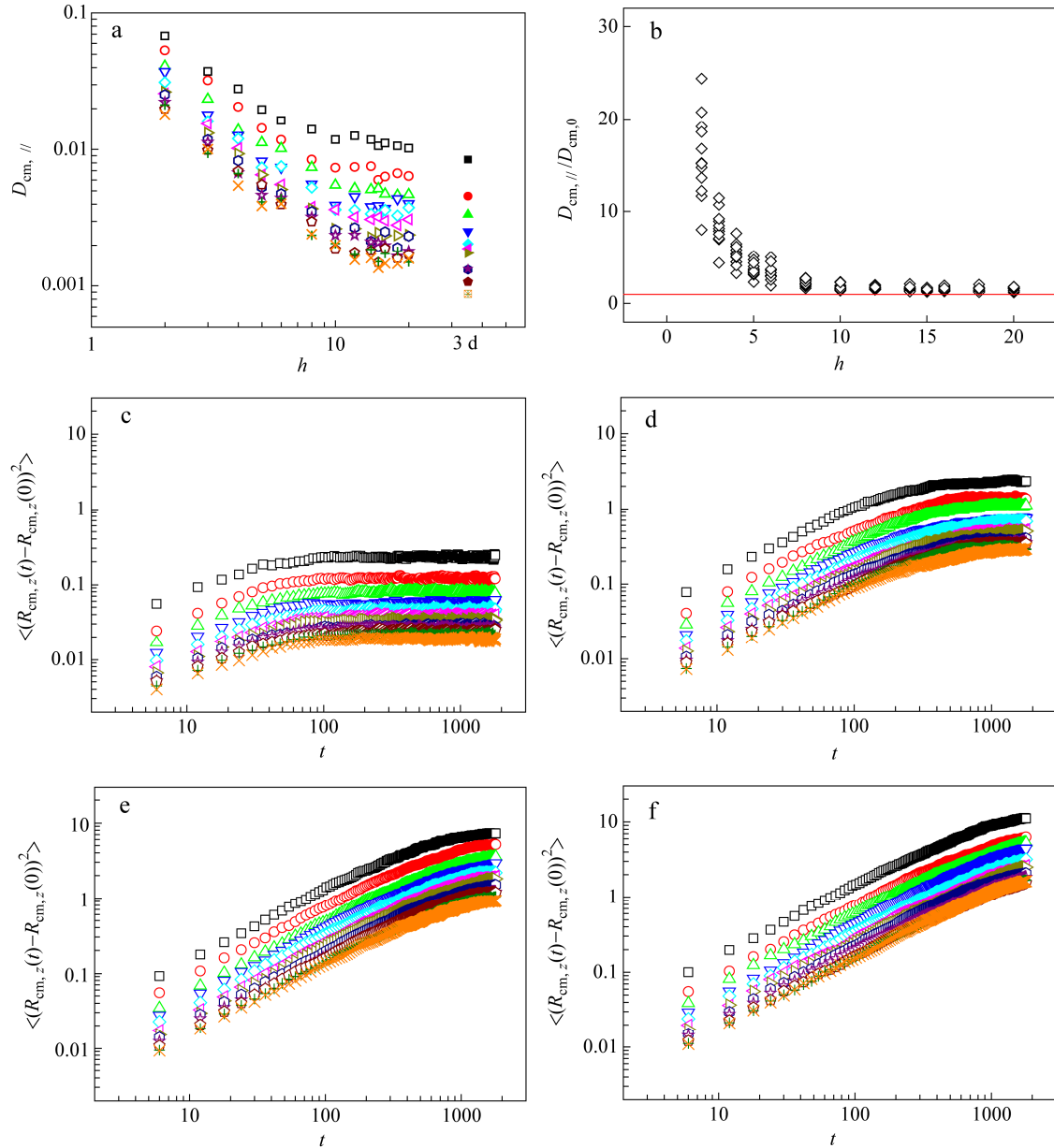


Fig. 3 (a) The h dependence of parallel diffusion coefficient of mass center $D_{\text{cm},//}$ of confined polymer chains; (b) The normalized $D_{\text{cm},//}/D_{\text{cm},0}$ of confined polymer chains plotted as functions of h ; (c, d, e, f) The z -direction mean square displacement of these polymer chains confined in a slit with $h = 2$ (c), 5 (d), 8 (e) and 10 (f) (The symbols have the same meaning as those in Fig. 2a.)

displacements at z -direction. For diffusion (Fig. 3b), there is no such a basin-like transition as occurring in the decay of $\langle R_g^2 \rangle$, which means the confinement shows different effects on the static and dynamic properties. In the following, we will give more information on the properties of single polymer chains influenced by the confinement and find the reason why the decay of the diffusion is of great difference from that of $\langle R_g^2 \rangle$.

Table 2. The h dependence of parallel diffusion coefficient $D_{cm, //} \times 10^3$ of the mass center of confined polymer chains (3d has the same meaning indicated in Table 1.)

$h \backslash N$	10	20	30	40	50	60	70	80	90	100	110	120
2.0	67.9	53.4	41.0	37.3	31.2	25.8	26.6	25.3	22.3	19.9	21.3	18.2
3.0	37.4	32.2	23.5	18.0	16.2	15.4	13.2	11.8	11.3	9.88	9.38	10.1
4.0	27.9	20.6	13.9	12.7	12.0	10.2	9.32	8.28	6.76	6.96	6.69	5.45
5.0	19.7	14.3	11.2	8.20	7.39	6.55	6.55	5.31	4.64	5.54	4.15	3.88
6.0	16.4	11.8	10.2	7.41	7.54	5.55	5.11	4.76	4.42	3.98	4.41	4.02
8.0	14.1	8.45	7.42	5.58	5.29	3.81	3.70	3.53	3.21	2.98	2.37	2.41
10.0	11.8	7.37	5.51	3.91	3.65	3.65	2.64	2.59	2.37	1.86	2.05	2.01
12.0	12.6	7.46	5.21	4.53	3.62	3.22	2.65	2.69	2.37	1.77	1.71	1.56
14.0	11.8	7.54	5.10	3.81	3.39	3.09	2.29	2.14	2.12	1.81	1.87	1.60
15.0	10.6	6.01	5.18	3.88	3.32	3.21	2.47	1.96	2.09	1.49	1.51	1.36
16.0	11.2	6.35	4.74	3.72	3.62	3.02	2.35	2.51	1.98	1.89	1.73	1.47
18.0	10.6	6.70	4.63	4.37	3.30	2.81	2.36	1.92	1.65	1.59	1.80	1.46
20.0	10.2	6.40	4.69	4.03	3.77	3.09	2.38	2.33	1.81	1.70	1.50	1.59
3d	8.45	4.57	3.35	2.53	2.05	1.89	1.75	1.32	1.33	1.07	0.873	0.877

It is assumed that a single chain confined in two plates will be compressed along the vertical direction and stretched along the parallel direction of the plates. So, to illustrate the change of the orientation for the confined polymer chain, we calculate the three components $\langle R_g^2 \rangle_x$, $\langle R_g^2 \rangle_y$, $\langle R_g^2 \rangle_z$ of $\langle R_g^2 \rangle$, which are normalized by $\langle R_g^2 \rangle_0/3$ ($\langle R_g^2 \rangle_0$ obtained in 3-dimensional unconfined systems)^[25] (Fig. 4a). When the distance is more than $ca. 5\langle R_g \rangle_0$, no apparent change can be found for the three components of $\langle R_g^2 \rangle$. While, when the distance is less than $ca. 5\langle R_g \rangle_0$, $\langle R_g^2 \rangle_z$ starts to reduce, and $\langle R_g^2 \rangle_x$, $\langle R_g^2 \rangle_y$ slightly increase, but the chain's size changes a little at the beginning, which means the decrease of h makes the confined polymer chain first orientate itself to be parallel to the plates. After that, further decreasing h will induce the great reduce of $\langle R_g^2 \rangle_z$ and the drastic increase of $\langle R_g^2 \rangle_x$ and $\langle R_g^2 \rangle_y$. Therefore, a minimum point of $\langle R_g^2 \rangle$ for the confined polymer chain is obtained and then followed by a drastic increase in $\langle R_g^2 \rangle$. The compression along z -direction makes the confined polymer stretch itself. According to Stokes-Einstein relation^[52, 53] $D = k_B T / 6\pi\eta R$, where η is solvent viscosity, the diffusion coefficient of a polymer chain is inversely proportional to its size, but this relation is obtained based on an assumption that the polymer chain could be treat as a sphere. While, as we know, the shape of single polymer chain in solvent is more like an ellipsoid^[40, 48]. So, here we introduce a tensor $\mathbf{Q}$ defined in Eq. (4) to quantitatively describe the shape change of a confined polymer chain. The ratios of three eigenvalues q_1, q_2, q_3 of tensor $\mathbf{Q}$ are obtained and normalized by the results in 3-dimensional unconfined systems for polymer chains with $N = 10 \sim 120$ confined in slits with different h . As is shown in Fig. 4(b), when h is higher than $ca. 4\langle R_g \rangle_0$, the shape of polymer chains only changes a little. For a smaller h (less than $ca. 4\langle R_g \rangle_0$), the polymer chain has to change its shape to adapt the increasing confinement imposed by the plates. With the decrease of $h/\langle R_g \rangle_0$, the polymer chain becomes a thicker ellipsoid first, which implies the shrinkage of the confined polymer chain, then followed by a shape change from a thick ellipsoid to a thin ellipsoid. The shape factor S can give better description of the shape for a given polymer chain^[54], which is defined as

$$S = 27 \frac{\prod_{i=1}^3 (q_i - \bar{q})}{(\text{tr} \mathbf{Q})^3} \quad (6)$$

where the negative values $-1/4 < S < 0$ of S correspond to oblate shapes and positive values $0 < S < 2$ represent prolate shapes. Figure 4(c) illustrates the $h/\langle R_g \rangle_0$ dependence of the shape of confined polymer chains. A

polymer chain behaves as a prolate ellipsoid in either weak or strong confined systems. And the basin-like behavior shown in Fig. 4(c) proves the results obtained from Fig. 4(b).

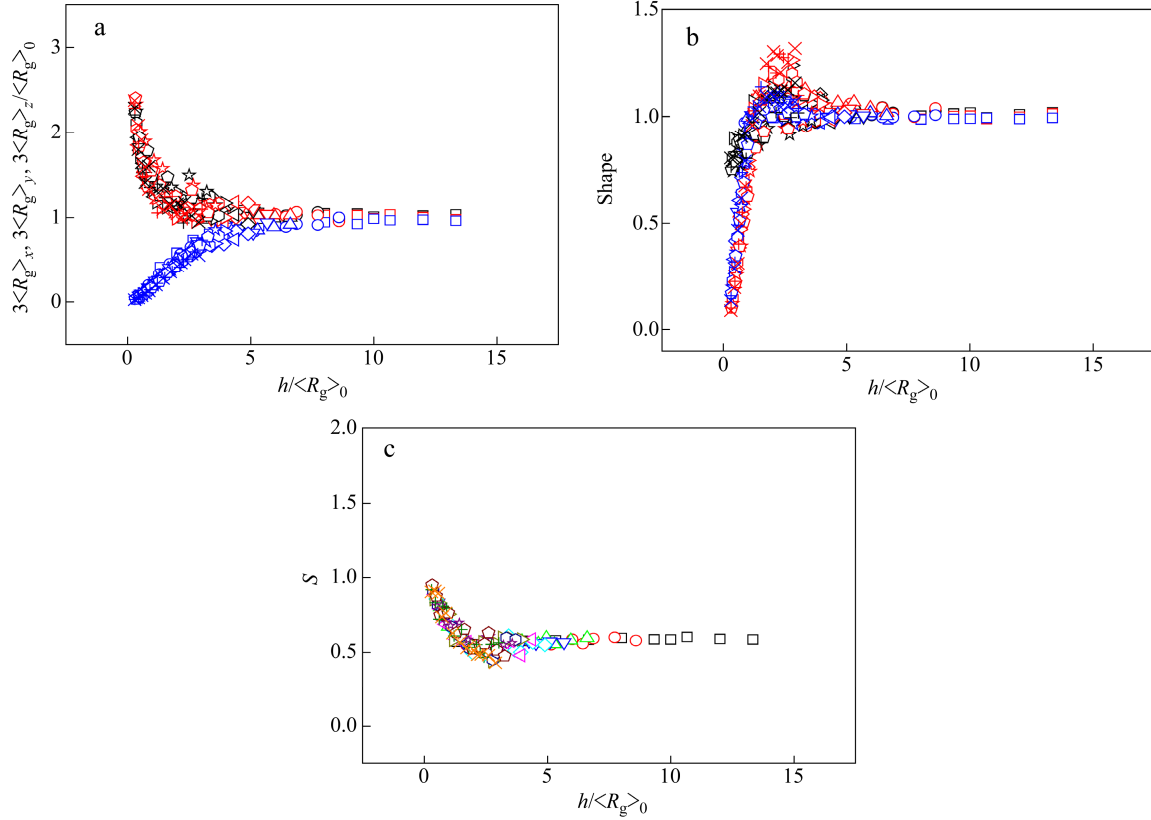


Fig. 4 (a) The normalized $3\langle R_g^2 \rangle_x / \langle R_g^2 \rangle_0$ (black), $3\langle R_g^2 \rangle_y / \langle R_g^2 \rangle_0$ (red) and $3\langle R_g^2 \rangle_z / \langle R_g^2 \rangle_0$ (blue) respectively plotted as functions of $h/\langle R_g \rangle_0$; (b) The $h/\langle R_g \rangle_0$ dependence of the normalized ratios $(q_2/q_1)/(q_2/q_1)_0$ (black), $(q_3/q_1)/(q_3/q_1)_0$ (red) and $(q_3/q_2)/(q_3/q_2)_0$ (blue) of the three normalized eigenvalues of the mass distribution tensor $\mathbf{Q}$; (c) The shape factors of confined polymer chains as functions of $h/\langle R_g \rangle_0$ (The symbols in Figs. 4a, 4b and 4c have the same meaning as in Fig. 2a.)

From the above discussion, we know that the distance between the two plates affects the molecular size, molecular shape and diffusion of the single confined polymer chain greatly. To get insight into these confined polymer chains, the pair distribution function^[41, 55] $G(r)$ of the polymer chain is investigated, which gives the probability of finding a pair of particles at distance r apart^[48]. If there are $n(r)$ particles between r and $r + \delta r$ from a given particle, the $G(r)$ is

$$G(r) = \frac{V}{N_{\text{tot}}} \left[\frac{n(r)}{4\pi r^2 \delta r} \right] \quad (7)$$

We have obtained the $G(r)$ of polymer chains with $N = 10$ –120 in slits with different h . Their $G(r)$ shows similar h dependence, thus, for convenience, we only show the $G(r)$ of the polymer chain of $N = 50$ in a slit with $h = 2, 5, 10$ and in an unconfined system in Fig. 5, where G_{PP} , or G_{PS} represents the probability of a monomer contacting its own chain or other solvent particles respectively, and $G_{\text{PS} + \text{PP}}$ denotes the total contact probability of the monomer. At small h , *i.e.* under strong confinement, the polymer chain mainly contacts solvent particles at short-range, and the long-range G_{PP} and G_{PS} are very small (Fig. 5a). With the increase of h , both short-range and long-range contact probabilities G_{PP} and G_{PS} increase. When h is large enough, both short-range and long-range

G_{PP} and G_{PS} are very close to those obtained in unconfined systems (Figs. 5b, 5c and 5d). However, the contact probability between polymer monomers G_{PP} shows a weaker h dependence than that of G_{PS} between polymer monomers and solvent particles. Similar results can also be clearly seen from the first peak G_m of $G(r)$ in Fig. 5(e) and the normalized value G_m/G_{m0} in Fig. 5(f) (G_{m0} is the corresponding result obtained from an unconfined system). In a 3-dimensional unconfined system, polymer chain has more probability to contact monomers of its own chain and solvent particles, which makes its motion strongly affected by the surrounding

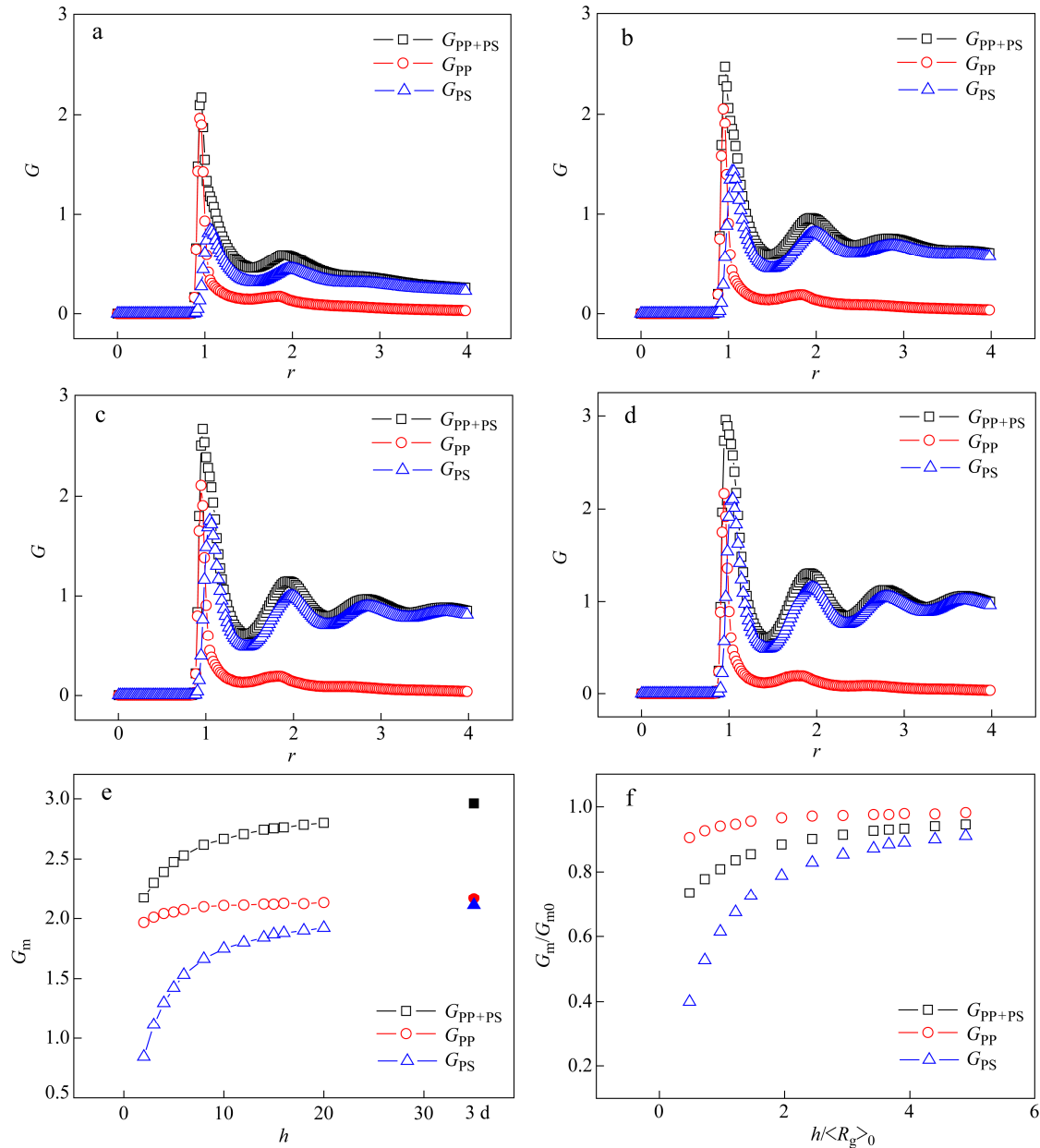


Fig. 5 The radial distribution function $G(r)$ of a single confined polymer chain with $N = 50$ in athermal solvent with $h = 2$ (a), 5 (b), 10 (c) and a single chain in a 3-dimensional unconfined system (d), and the h dependence of the value G_m of the first peak of $G(r)$ (e) and the $h/\langle R_g \rangle_0$ dependence of its normalized value G_m/G_{m0} (f). G_{PP} and G_{PS} respectively represent the probability of a monomer contacting monomers of its own chain or solvent particles, while G_{PP+PS} means the total contact probability of a polymer monomer, where the solid symbols in Fig. 5(e) represent the data obtained from 3-dimensional unconfined systems.

particles so that the whole polymer chain has a slow diffusion. Slightly increasing the degree of confinement, *i.e.*, h is in the range of *ca.* $2.0\langle R_g \rangle_0$ to *ca.* $4.0\langle R_g \rangle_0$, G_{PP} , G_{PS} , and G_{PS+PP} only show a little decrease compared with the results gained with three dimensional unconfined conditions. In this region, the polymer feels the confinement from the plates, but it can adapt the existence of confinement by reorienting its shape to be parallel to the plates or partly changing its shape, so its size and shape only change a little. With further decreasing h (less than *ca.* $2.0\langle R_g \rangle_0$), G_{PP} , G_{PS} , and G_{PS+PP} show a great difference from their three dimensional value. In this region, a decrease of h increases the degree of confinement greatly, and the polymer chain has less probability to contact other particles. So, the motion of polymer is weakly affected by the surrounding particles, and therefore, the diffusion of polymer chain is accelerated and shows a faster diffusion behavior. Correspondingly, there is a drastical increment for the diffusion coefficient of a polymer chain when it is of strong confinement. The pair distribution function gives a better description of the reason why the diffusion behavior does not show similar decay behavior as that of $\langle R_g^2 \rangle$.

Besides, we also share our attentions to the scaling relationship of confined polymers. As is known, the properties of polymers depend on the space dimension^[37, 56, 57]. Flory^[58] gave that the static scale exponent of polymers in dilute solution follows the relationship of $\nu = 3/(d + 2)$, subsequently, $\nu = 3/5$ in 3-dimensional systems and $\nu = 3/4$ in 2-dimensional systems. So it is necessary to give the static scale relationship of polymer chains in the systems being between 2-dimension and 3-dimension. In this work, the confined single polymer chain behaves as a free chain in a 3-dimensional system for very weak confined (very large h) systems and has a similar behavior as that in a 2-dimensional system for very strong confined (very small h) systems. This system supplies us an opportunity to reveal the h dependence of the static scale exponent ν of polymer chains in solution. The static scale exponent ν is given in Fig. 6(a) and listed in Table 3 obtained by the mean square radius of gyration of confined polymer chains with $N = 10$ –120 (Fig. 6b). We gain $\nu_{3d} = 0.59$ in 3-dimensional unconfined systems which is in agreement with experiment and Flory's exponent^[58]. Obviously, the static scale exponent ν shows a clear h dependence. It decreases quickly with the increase of h until reaching a region, where ν slightly less than ν_{3d} , after that, ν starts to increase and tend to the result of 3-dimensional unconfined systems.

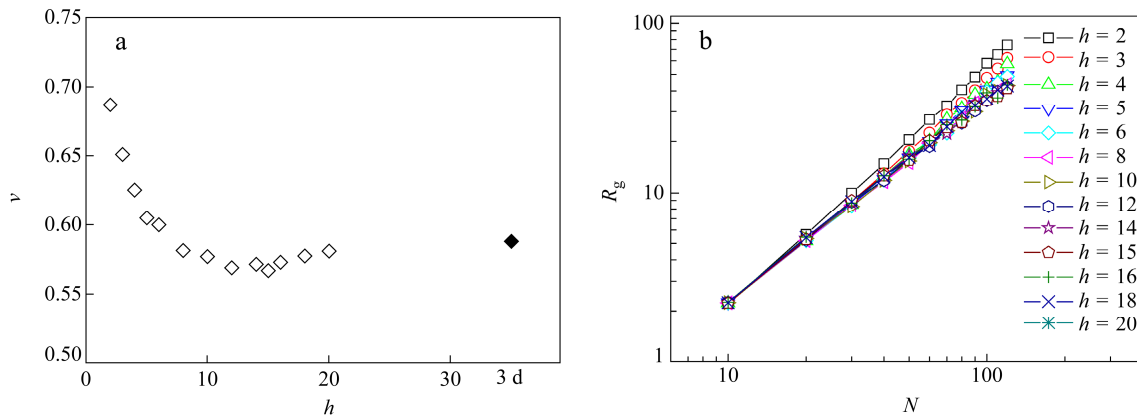


Fig. 6 (a) The h dependence of the static scale exponent ν of the confined polymer chains (The solid symbol also represents that these data are obtained from 3-dimensional unconfined systems.); (b) The mean square radius of gyration $\langle R_g^2 \rangle$ of the single confined polymer chain with $N = 10$ –120 of $h = 2$ ($\square$), 3 ($\circ$), 4 ($\triangle$), 5 (∇), 6 ($\diamond$), 8 ($\triangleleft$), 10 ($\triangleright$), 12 ($\circ$), 14 ($\star$), 15 ($\circ$), 16 ($+$), 18 ($\times$) and 20 ($\ast$)

Because of the result proved above, that the confined behavior of polymer chain relies on its length, so we gain the static scale exponent ν' of single confined polymer chains with the same degree of confinement, *i.e.* equal $h/\langle R_g \rangle_0$, and list them in Table 4. Due to the limitations of a constant number density and a high computational efficiency, we only obtain ν' for $h/\langle R_g \rangle_0 = 0.6, 1.3, 2.0, 2.6$. It is interesting that the ν' values obtained from these four kinds of confined systems are very similar and all close to ν_{3d} , even for the more strongly confined

system of $h/\langle R_g \rangle_0 = 0.6$. This interesting phenomenon was also observed by Romiszowski *et al.*^[23, 29]. But so far, we could not give a clear explanation.

Table 3. The static scaling exponent ν of a single polymer chain confined in a slit formed by two parallel plates with a distance of h apart (3d has the same meaning as in Table 1.)

h	2.0	3.0	4.0	5.0	6.0	8.0	10.0
ν	0.69	0.65	0.63	0.60	0.60	0.58	0.58
h	12.0	14.0	15.0	16.0	18.0	20.0	3d
ν	0.57	0.57	0.57	0.57	0.58	0.58	0.59

Table 4. The static scale exponent ν' of a single confined polymer chain with the same $h/\langle R_g \rangle_0$

$h/\langle R_g \rangle_0$	0.6	1.3	2.0	2.6
ν'	0.59	0.58	0.57	0.58

SUMMARY

We have investigated the static and dynamic properties of a single polymer chain confined in a slit formed by two parallel plates with different distances h . It is found that the molecular sizes, shapes, and diffusion behaviors of confined polymer chains strongly depend on h . With the increase of h , the mean square radii of gyration and diffusion coefficients of mass center for confined polymer chains show special decay behaviors respectively, and a universal law about the $h/\langle R_g \rangle_0$ dependence of the static properties of single confined polymer chains is obtained. It is supposed that the increasing degree of confinement makes polymer chain first parallel itself to the plates, then squeeze itself like a thick ellipsoid, and finally stretch itself to be adapted to the variation of the confined systems by studying the shape of polymer. Moreover, we give a better explanation for the reason why the decay of diffusion shows a behavior different from that of polymer chain size. Namely, the decay behavior of the diffusion of a confined polymer chain is dominated by the contact probability between a monomer and other monomers or solvent particles, and the contact probability monotonically decreases with decreasing h . While, for the decay of the polymer size, a confined polymer chain could adopt two approaches to cater to the compression of the parallel plates, *i.e.* orientation and shape changing. So, there is a basin-like region in the decay curve of the polymer chain size, and no such a basin is found in the decay curve of the polymer chain diffusion. These results may help us have a better understanding of the static and dynamic properties of single polymer chains under confinement.

REFERENCES

- 1 Wang, Y. and Teraoka, I., *Macromolecules*, 2000, 33: 3478
- 2 Cacciuto, A. and Luijten, E., *Nano Lett.*, 2006, 6: 901
- 3 Chou, C.F., Austin, R.H., Bakajin, O., Tegenfeldt, J.O., Castelino, J.A., Chan, S.S., Cox, E.C., Craighead, H., Darnton, N., Duke, T., Han, J. and Turner, S., *ElectroPhoresis*, 2000, 21: 81
- 4 Pra, M.D., Kok, W.T. and Schoenmakers, P.J., *J. Chromatogr. A*, 2008, 1184: 560
- 5 Han, J., Fu, J. and Schoch, R.B., *Lab on a Chip*, 2007, 8: 23
- 6 Ma, W., Banavar, J.R. and Koplik, J., *J. Chem. Phys.*, 1992, 97: 485
- 7 Zhu, W., Li, W. and Ma, H., *Chinese J. Chem. Phys.*, 2002, 15: 295
- 8 Wei, D., Yang, W., Jin, X. and Liao, Q., *J. Chem. Phys.*, 2007, 126: 204901
- 9 Oleinikova, A. and Brovchenko, I., *Phys. Rev. E*, 2007, 76: 041603
- 10 He, Y., Qian, H., Lu, Z. and Li, Z., *Polymer*, 2007, 48: 3601
- 11 Shaffer, J.S., *Macromolecules*, 1996, 29: 1010
- 12 Nie, Z., Su, Z., Sun, Z., Shi, T. and An, L., *Macromol. Theory Simul.*, 2005, 14: 463

- 13 Cordeiro, C.E., *J. Phys. Chem. Solids*, 1999, 60: 1645
- 14 Chen, S.B., *J. Chem. Phys.*, 2005, 123: 074702
- 15 Hsu, H.P. and Grassberger, P., *J. Chem. Phys.*, 2004, 120: 2034
- 16 Morrison, G. and Thirumalai, D., *J. Chem. Phys.*, 2005, 122: 194907
- 17 Romiszowski, P. and Sikorski, A., *Monatshefte Fur Chemie*, 2006, 137: 969
- 18 Sikorski, A. and Romiszowski, P., *J. Chem. Phys.*, 2004, 120: 7206
- 19 Romiszowski, P. and Sikorski, A., *J. Molecular Modeling*, 2005, 11: 335
- 20 van Vliet, J.H., Luyten, M.C. and ten Brinke, G., *Macromolecules*, 1992, 25: 3802
- 21 van Vliet, J.H. and ten Brinke, G., *J. Chem. Phys.*, 1990, 93: 1436
- 22 van Vliet, J.H. and ten Brinke, G., *Macromolecules*, 1992, 25: 3695
- 23 Romiszowski, P. and Sikorski, A., *Physica A — Statistical Mechanics and Its Applications*, 2005, 357: 356
- 24 Chen, Y.L., Graham, M.D., de Pablo, J.J., Randall, G.C., Gupta, M. and Doyle, P.S., *Phys. Rev. E*, 2004, 70: 4
- 25 Chaudhuri, D. and Mulder, B., *Phys. Rev. E.*, 2011, 83: 031803
- 26 Cifra, P., *J. Chem. Phys.*, 2009, 131: 224903
- 27 Soong, R. and Macdonald, P.M., *Langmuir*, 2008, 24: 518
- 28 Dimitrov, D.I., Milchev, A., Binder, K., Klushin, L.I. and Skvortsov, A.M., *J. Chem. Phys.*, 2008, 128: 234902
- 29 Romiszowski, P. and Sikorski, A., *Acta Physica Polonica B*, 2004, 35: 1535
- 30 Uemura, H., Ichikawa, M. and Kimura, Y., *Phys. Rev. E*, 2010, 81: 051801
- 31 Hsieh, C.C., Balducci, A. and Doyle, P.S., *Macromolecules*, 2007, 40: 5196
- 32 Bonthuis, D.J., Meyer, C., Stein, D. and Dekker, C., *Phys. Rev. Lett.*, 2008, 101: 108303
- 33 Tang, J., Levy, S.L., Trahan, D.W., Jones, J.J., Craighead, H.G. and Doyle, P.S., *Macromolecules*, 2010, 43: 7368
- 34 Brochard, F. and de Gennes, P.G., *J. Chem. Phys.*, 1977, 67: 52
- 35 Milchev, A. and Binder, K., *J. De Physique II*, 1996, 6: 21
- 36 Hagita, K., Koseki, S. and Takano, H., *J. Phys. Society Japan*, 1999, 68: 2144
- 37 Cui, T., Ding, J. and Chen, J.Z.Y., *Phys. Rev. E.*, 2008, 78: 061802
- 38 Kalb, J. and Chakraborty, B., *arXiv:cond-mat*, 2008, 0702152
- 39 Allen, M.P. and Tildesley, D.J., “Computer simulation of liquids”, Clarendon, Oxford, 1987
- 40 Fu, C., Ouyang, W., Sun, Z. and An, L., *J. Chem. Phys.*, 2007, 127: 044903
- 41 Rappaport, D.C., “The art of molecular dynamics simulation”, Cambridge University Press, Cambridge, 1997
- 42 Starr, F.W., Schroder, T.B. and Glotzer, S.C., *Macromolecules*, 2002, 35: 4481
- 43 Galliero, G. and Volz, S., *J. Chem. Phys.*, 2008, 128: 064505
- 44 Fu, C., Sun, Z., Li, H., An, L. and Tong, Z., *Polymer*, 2008, 49: 3832
- 45 Luo, M.B., *Polymer*, 2007, 48: 7679
- 46 Berendsen, H.J.C., Postma, J.P.M., van Gunsteren, W.F., DiNola, A. and Haak, J.R., *J. Chem. Phys.*, 1984, 81: 3684
- 47 Dünweg, B. and Kremer, K., *J. Chem. Phys.*, 1993, 99: 6983
- 48 Fu, C., Ouyang, W., Sun, Z., An, L., Li, H. and Tong, Z., *Polymer*, 2009, 50: 5142
- 49 Jeon, J. and Chun, M.S., *J. Chem. Phys.*, 2007, 126: 154904
- 50 Cifra, P. and Bleha, T., *Macromol. Theory Simul.*, 2000, 9: 555
- 51 Chen, Y., Wang, C. and Luo, M., *Acta Polymerica Sinica (in Chinese)* 2010, (9): 1082
- 52 Rubinstein, M. and Colby, R.H., “Polymer physics”, Oxford University Press, Oxford, 2003
- 53 Milchev, A. and Binder, K., *Europhys. Lett.*, 1994, 26: 671
- 54 Dima, R.I. and Thirumalai, D.J., *Phys. Chem. B*, 2004, 108: 6564
- 55 Rahman, A., *Phys. Rev.*, 1964, 136: 405
- 56 Rudnick, J., Beldjenna, A. and Gaspari, G., *J. Phys. A: Math. Gen.*, 1987, 20: 971
- 57 Bishop, M. and Saltiel, C.J., *J. Chem. Phys.*, 1987, 88: 3976
- 58 de Gennes, P.G., “Scaling concepts in polymer physics”, Cornell University, Ithaca and London, 1979