

STIFFNESS AND EXCLUDED VOLUME EFFECTS ON CONFORMATION AND DYNAMICS OF POLYMERS: A SIMULATION STUDY*

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Abstract This work investigates the effects of the excluded volume and especially those of the chain stiffness on the structural and dynamical properties of a model polymer chain. The theoretical framework is the same as in the recent works by Steinhauser *et al.*, where a Rouse approach is adopted. Our model differs in that our chains have a finite average bending angle. As in the works by Steinhauser *et al.*, Langevin dynamic simulations were performed without hydrodynamic interactions. Whereas this doesn't impact the static properties we obtain, it also allows us to compare our results on dynamic properties to those predicted by Rouse theory, where hydrodynamic interactions are also neglected. Our results show that the structural properties are very sensitive to the chain stiffness, whereas the dynamic scaling laws remain the same as those by Rouse theory, with the prefactor depending on the persistence length.

Keywords: Scaling laws; Polymer; Stiffness; Excluded volume effects.

INTRODUCTION

Static and dynamic properties of polymer chains are crucial to the understanding of polymeric materials. Scaling laws play a central role in the understanding and characterization of linear polymers in dilute solutions at equilibrium^[1, 2]. Many of the observable static and dynamic properties of polymers in dilute solutions are well characterized by scaling laws^[3]. If A is an observable physical quantity, when the number of monomers N is large, the physical quantities which determine the overall properties of chain satisfy the relationship $A \sim N^\nu \sim L^\nu$. Here L is the contour length of the polymer and ν is the scaling exponent which is independent of local molecular structure of the polymer. For example, for radius of gyration R_g , scaling arguments show $R_g \propto (N-1)^\nu$. The static exponent is equal to 0.5 for ideal chains in any space dimension, and is approximately 0.6 for real chains in 3 dimensions. This result has been verified by light scattering experiments^[1].

The typical ideal chain model, the Gaussian chain, only takes into account short range elastic interactions which occur between neighboring monomers along the chain. The bonds which are described by linear elastic forces are not forbidden from passing through each other. Unlike ideal chains, a real chain has excluded volume interaction which is important for real polymer chains in good solvents, and a real chain is subject to bond bending, rotational and torsional angles constraints, therefore has local rigidity. Chain stiffness has been shown

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to influence the structure and dynamics of system^[2-6]. In simulation of polymers, finitely extensible nonlinear elastic (FENE) potential is frequently used^[7, 8]. It has been shown that the structural properties and the dynamics of real polymers are well described by the FENE model. For modeling a polymer chain with excluded volume interaction and chain stiffness, we here introduce Weeks-Chander-Anderson (WCA) potential, bending potential and finitely extensible nonlinear elastic (FENE) potential to model excluded volume interactions, chain stiffness and chain connection respectively.

Considerable theoretical works and computer simulations have been devoted to scaling properties of polymers. de Gennes and Pincus^[9, 10] did scaling analysis on the static properties of deformed, isolated, flexible polymers in limit of weak and strong forces, respectively. Odijk^[11] formulated scaling relations for semidilute polyelectrolyte solutions. Webman *et al.*^[12] and Wittkop *et al.*^[13] executed computer simulations with lattice models to test scaling laws. Pierleoni *et al.*^[14] studied scaling of chains in good solvents undergoing steady shear flow by molecular dynamics. Dobrynin^[15] extended and generalized the scaling picture of de Gennes *et al.* and Pfeuty^[16] to both unentangled and entangled regimes of flexible polyelectrolyte solutions. Sheng *et al.*^[17] used a bead-spring model in continuous space to discuss the scaling laws in detail. Spenley^[18] performed scaling laws for polymer in dilute solution and in the melt with dissipative particle dynamics (DPD). Steinhäuser^[5] used Langevin dynamic simulations to examine static and dynamic scaling of semiflexible polymer chains in melts. Steinhäuser *et al.*^[6] performed Langevin dynamic simulations to study dynamic crossover behavior of semiflexible linear polymers in solution and in the melt.

Although excluded volume effects and chain stiffness in dilute polymer solutions have already been studied by many previous works, it seems still interesting to characterize the influence of the chain stiffness on the scaling laws of excluded volume chains, especially for semi-flexible chains with finite equilibrium bond angle. The present work is a study of the scaling properties of such semi-flexible polymer chains with excluded volume effects and stiffness in good dilute solvents simulated by Langevin dynamics. The hydrodynamic interactions are not taken into consideration in the present work.

SIMULATION METHOD

Polymer chains are studied in this work by using the FENE bead-spring model. Langevin dynamic simulations are employed. The dynamics of the i th bead is described by Langevin equation:

$$m\dot{v}_i(t) = F_i(t) - m_i\gamma_i v_i(t) + R_i(t) \quad (1)$$

where $v_i(t)$ is the velocity of bead i with mass m_i at time t , $F_i(t)$ is the systematic force, γ_i defines the friction coefficient and $R_i(t)$ is a random force acting on bead i due to the motion of solvent molecules, which is stipulated to satisfy following relationship:

$$\langle R_{i\alpha}(t)R_{j\beta}(t') \rangle = 2m_i\gamma_i k_B T_0 \delta_{ij} \delta_{\alpha\beta} \delta(t-t') \quad (2)$$

where the symbol $\langle \cdot \rangle$ means an equilibrium average, k_B is the Boltzmann constant and T_0 is the target temperature. The Greek-letter subscripts denote x , y , or z components. An adapted velocity Verlet finite-differencing scheme is used for integration of Langevin equation. The details of this algorithm are presented elsewhere^[19].

For polymer chains with excluded volume effects, all non-bonded pairs of beads in the system interact *via* a short-range repulsive Weeks-Chander-Anderson (WCA) potential^[20], while the interaction between bonded beads are built as the sum of WCA potential and FENE potential. By using such a potential, the excluded volume effects are represented and the properties of real polymer chains can be studied^[21].

The WCA potential is the Lennard-Jones potential truncated at the position of the minimum and shifted to eliminate the discontinuity:

$$U_{ij}^{\text{WCA}} = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] + \epsilon & \text{for } r_{ij} \leq 2^{1/6} \sigma, \\ 0 & \text{for } r_{ij} > 2^{1/6} \sigma \end{cases} \quad (3)$$

where r_{ij} is the distance between beads i and j , ϵ is the Lennard-Jones energy parameter (potential well depth) and σ is the Lennard-Jones length parameter (effective diameter of beads). The WCA potential results in a purely repulsive potential that includes the effects of excluded volume.

The FENE potential is given by:

$$U_{ij}^{\text{FENE}} = \begin{cases} -\frac{1}{2} k R_0^2 \ln \left(1 - \frac{r_{ij}^2}{R_0^2} \right) & \text{for } r_{ij} < R_0, \\ 0 & \text{for } r_{ij} \geq R_0 \end{cases} \quad (4)$$

where R_0 is a finite extensibility distance and k is a spring constant. The FENE potential in conjunction with the WCA purely repulsive interaction forms a potential well for the flexible bonds that maintains the topology of the molecules. In this work the FENE parameters were set to $R_0 = 1.5\sigma$ and $k = 30\epsilon/\sigma^2$. For this choice of parameters the maximal extension of bonds is short enough to prevent crossing of beads, whereas the magnitude of the bonding force is small enough to enable simulations with relatively large time steps^[22].

To model the stiffness of polymer chains, a bending potential^[23] is added into the interactions of neighboring beads beside WCA potential and FENE potential. The bending potential between two successive bonds is taken as:

$$U_{\text{bending}} = K_\theta (\theta - \theta_0)^2 \quad (5)$$

where θ is the bond angle between two successive bond vectors. θ_0 is the equilibrium bond angle, which is set as 150° in the simulations. K_θ is the bending force constant, which is ranging from 0 to 600 in the simulations to study the effects of chain stiffness.

No periodic boundary condition is applied in the simulation system in order to model dilute solutions. The number of beads N is varied between 8 and 200. All physical quantities are expressed in the standard Lennard-Jones (LJ) units. The mass of polymeric beads is set as unit mass, so that reduced unit for time is described as $t^* = \sqrt{m\sigma^2/\epsilon} = \sqrt{\sigma^2/\epsilon}$ by LJ units.

The equations of motion were integrated using the adapted velocity Verlet method, and the time step was 0.005. The system has been pre-equilibrated for a number of steps equal to 1×10^7 for chains of $N \leq 100$ and 1×10^8 for chains of $N > 100$. Production runs have been followed by similar steps of 1×10^8 .

RESULTS AND DISCUSSION

Excluded Volume Effects on Flexible Chains with Only Excluded Volume Effects

In the simulations of the first case, bending force constant K_θ is set as 0 to model flexible chains with only excluded volume effects (no stiffness). The root-mean-square end-to-end distance R_0 , radius of gyration R_g , rotational relaxation time τ_r and diffusion coefficient of the center-of-mass D are calculated.

The autocorrelation function of the end-to-end vector $\langle \mathbf{R}_e(t) \cdot \mathbf{R}_e(0) \rangle$, where $\mathbf{R}_e$ is the end-to-end vector, is asymptotically an exponential function of t , and the rotational relaxation time τ_r is extracted by fitting at long times. The diffusion coefficient of center-of-mass D is measured by calculating the mean-square displacement of the center-of-mass coordinate $\langle (\mathbf{R}_{\text{cm}}(t) - \mathbf{R}_{\text{cm}}(0))^2 \rangle$ which tends to be $6Dt$ for time longer than τ_r .

The measured quantities R_0 , R_g , τ_r and D are shown as $K_\theta = 0$ cases in Fig. 1. R_0 and R_g are shown as a function of $N - 1$, while τ_r and D are plotted against N . A fitting by power law function $y = ax^b$ of R_0 versus $N - 1$, and τ_r and D versus N were performed. The fitting results are shown as dash lines on the graphs, and are

numerically as follows:

$$R_0 = (1.23 \pm 0.09)(N-1)^{0.59 \pm 0.02} \quad (6)$$

$$\tau_r = (1.0 \pm 0.6)N^{2.1 \pm 0.2} \quad (7)$$

$$D = (0.162 \pm 0.004)N^{-0.97 \pm 0.01} \quad (8)$$

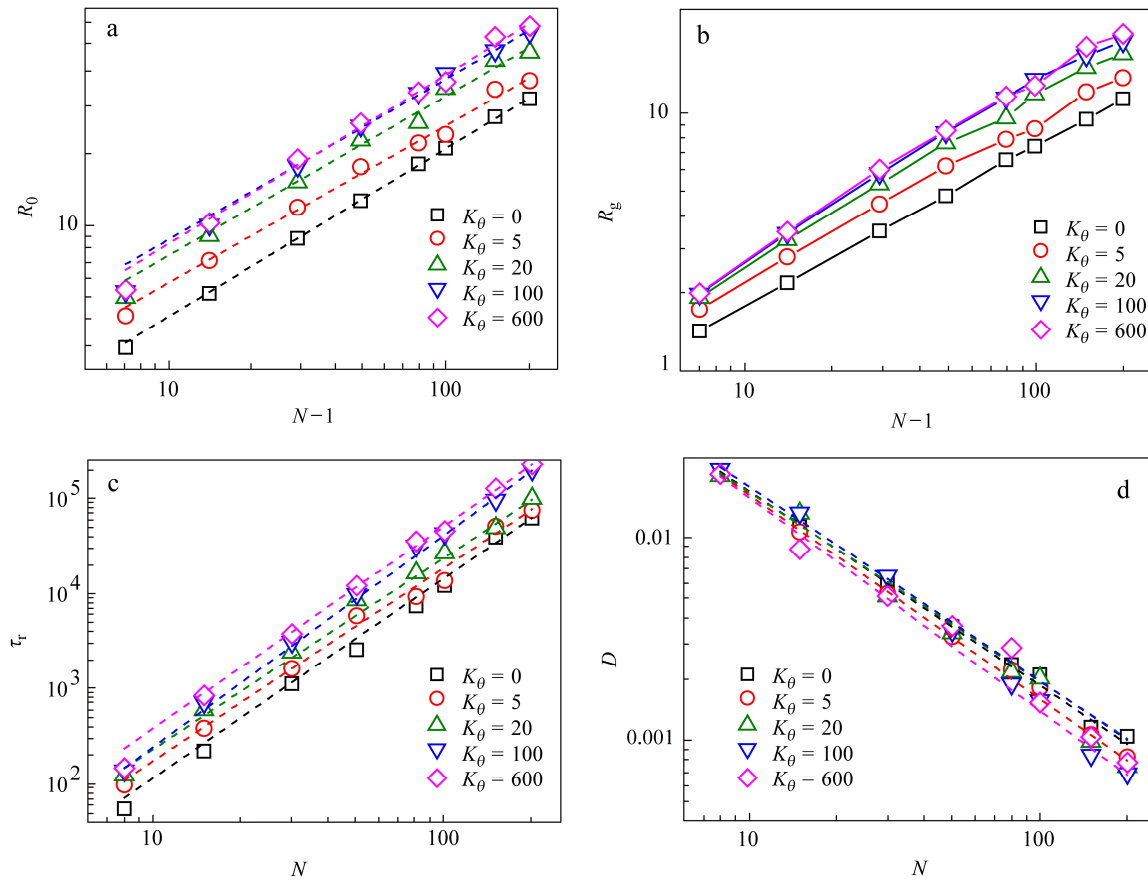


Fig. 1 (a) Root-mean-square end-to-end distance R_0 versus $N - 1$, (b) radius of gyration versus $N - 1$, (c) rotational relaxation time τ_r versus N and (d) diffusion coefficient of center-of-mass D versus N (N is the number of monomers in the polymer chains. Bending force constant $K_\theta = 0, 5, 20, 100$ and 600 . The dashed lines are fitted by power law function $y = ax^b$.)

The static exponent 0.59 ± 0.02 between R_0 (R_g) and $N - 1$ is approximately equal to 0.6 for real chains, while it is 0.5 in the Rouse model. Both the slopes of τ_r and D versus N are close to theoretical value 2.2 and -1 of Rouse model, respectively.

The difference between exponent 0.59 from our result (Eq. (6)) and 0.5 from ideal chain Rouse model is the effects of the excluded volume interactions, which is represented as WCA + FENE potential between beads instead of the simple form potential of Hookean springs. The WCA + FENE potential prevents crossing of beads, so that the exponent of R_0 versus $N - 1$ is different from that of ideal chain Rouse model. Meanwhile, it is to be noted that the exponent of D versus N agrees well with ideal chain Rouse model, which means the excluded volume effects do not affect scaling behaviors of this property. Our result for τ_r is consistent with the scaling prediction $\tau_r \propto N^{1+2\nu}$, based on the Rouse model in good solvents ($\nu = 0.6$).

Effects of Chain Stiffness on Dynamic Properties

In the second case, bending force constant K_θ is set as 5, 20, 100 and 600 to model different stiffness. R_0 , R_g , τ_r , and D are also measured and plotted in Fig. 1. The fitting results by power law function $y = ax^b$ are shown as lines on the graphs, and are numerically shown in Table 1.

Table 1. Numerical fitting results of R_0 , R_g , τ_r , and D to $N-1$ or N by power law function $y = ax^b$

K_θ	R_0	τ_r	D
5	$(1.7 \pm 0.3)(N-1)^{(0.57 \pm 0.03)}$	$(1.6 \pm 1.7)N^{(2.0 \pm 0.2)}$	$(0.17 \pm 0.01)N^{(-1.02 \pm 0.02)}$
20	$(2.1 \pm 0.4)(N-1)^{(0.58 \pm 0.04)}$	$(2.2 \pm 1.3)N^{(2.0 \pm 0.2)}$	$(0.15 \pm 0.02)N^{(-0.94 \pm 0.06)}$
100	$(2.3 \pm 0.2)(N-1)^{(0.58 \pm 0.02)}$	$(2.2 \pm 0.7)N^{(2.1 \pm 0.1)}$	$(0.17 \pm 0.02)N^{(-0.96 \pm 0.04)}$
600	$(2.1 \pm 0.3)(N-1)^{(0.61 \pm 0.03)}$	$(2.8 \pm 0.8)N^{(2.1 \pm 0.1)}$	$(0.19 \pm 0.04)N^{(-1.06 \pm 0.08)}$

The results in Fig. 1 show that all intercepts in the second case are larger than those in the first case, and all slopes in both cases are very close. The slopes between R_0 and $N-1$ in both cases are fixed at 0.6. The slope of τ_r are 2.0, 2.0, 2.1 and 2.1 when $K_\theta = 5, 20, 100$ and 600, respectively, therefore it varies slightly from 2.1 of $K_\theta = 0$. In all cases the exponent for D is very close to -1 .

It can be seen that the scaling exponents of τ_r and D are in quite satisfactory agreement with those of Rouse model, indicating that chain stiffness doesn't influence these dynamic scaling properties of the model.

The essence of the Rouse model is in the universal nature of the modeling of the dynamics of a connected object, and the central assumption in the Rouse model is that the dynamics is governed by the interactions that are localized along the chain. Chain stiffness also belongs to short range interactions; the essence of our model's potential is not changed although bending potential was added. So it is not surprising that the scaling exponents of τ_r and D , which characterize the global chain dynamic properties, are not changed from the first case. By contrast, intra-chain modes can be sensitive to the bending stiffness, as shown for example by Steinhauser^[5]. Other examples are the static structural properties investigated in the next section.

Static Structural Properties

Chain stiffness strongly affects the bond auto-correlation and thus the persistence length. Our model resembles the freely rotating chain model that assumes that all bond lengths and bond angles are fixed (constant) and all torsion angles are equally likely and independent of each other. The differences between our model and freely rotating chain model are that our model allows bond length l and bond angle θ to fluctuate around some fixed values.

The correlation between bond vectors $\mathbf{r}_i$ and $\mathbf{r}_j$ is passed along through the chain of bonds connecting bonds $\mathbf{r}_i$ and $\mathbf{r}_j$. For freely rotating chain, the component of $\mathbf{r}_j$ normal to vector $\mathbf{r}_{j-1}$ averages to zero due to free rotations of the torsion angle. The only correlation between bond vectors which is transmitted down the chain is the tangential component. Therefore, the correlation between bond vectors $\mathbf{r}_i$ and $\mathbf{r}_j$ is^[2]

$$\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = l^2 (\cos \theta)^{|j-i|} = l^2 \exp[|j-i| \ln(\cos \theta)] = l^2 \exp\left[-\frac{|j-i|}{s_p}\right] \quad (9)$$

The average $\langle \cdot \rangle$ indicates an average over all possible states of the system. The final relation defines s_p as the number of main-chain bonds in a persistence segment, which is the scale at which local correlations between bond vectors decay:

$$s_p = -\frac{1}{\ln|\cos \theta|} \quad (10)$$

The persistence length is the length of this persistence segment:

$$l_p = s_p l \quad (11)$$

where θ is bond angle, l is bond length.

To examine impact of chain stiffness on bond auto-correlation and persistence length, bond auto-correlations versus $|j - i|$ were drawn in Fig. 2. The persistence length l_p was obtained by fitting the bond auto-correlation function with function $y = ae^{bx}$ (according to Eq. (9)), and plotted in Fig. 3 as a function of K_θ . Figure 2 shows with the increase of K_θ the steepness of curves decreases, but that the decline rate of steepness of curves also decreases. When K_θ is over 100, all curves almost coincide (simulations with $K_\theta = 200, 300, 400, 500$ were performed, but the results were not shown in Fig. 2 for clarity). The steepness of curve reflects the decay rate of bond auto-correlation. The bigger the steepness, the more rapidly bond auto-correlation decay. This can explain the fact that the bigger K_θ is, the farther the correlation pass along through the chain. The saturation effect observed for $K_\theta > 100$ indicates that the fluctuations of the bond angle become very small for these stiffness values, so that our model approaches the freely rotating chain model, the decay of the bond auto-correlation thus follows Eq. (9) with the persistence length given by Eq. (10) with $\theta = 150^\circ$. The fitted persistence lengths l_p were plotted in Fig. 3 as a function of K_θ for $N = 100$. Indeed, we observed in Fig. 3, the rapid increase of l_p for $K_\theta < 100$ is followed by a plateau value for $K_\theta > 100$, which is given approximately by

$$\frac{1}{\left| \ln |\cos(150^\circ)| \right|} = 6.95.$$

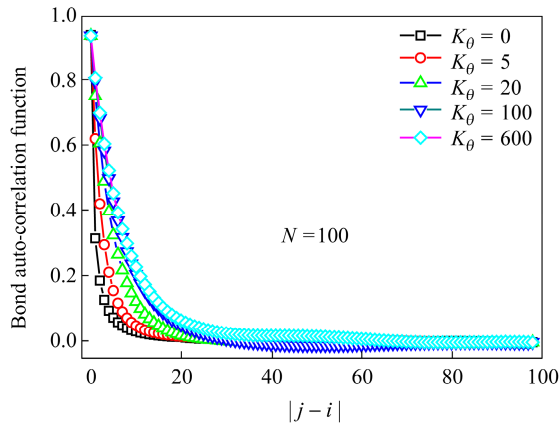


Fig. 2 Bond auto-correlation curves for $N = 100$ under various K_θ values

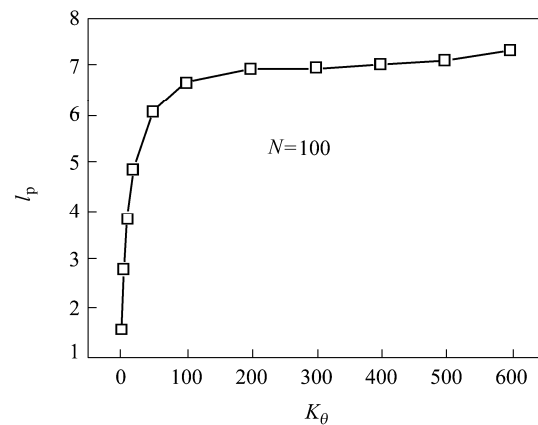


Fig. 3 Persistence length l_p as a function of K_θ for $N = 100$

The pair correlation function $g(r)$ is the probability density of finding one monomer at distance r when another is fixed at the origin. The pair correlation function is useful because it provides insight into the microscopic structure. Figure 4 shows $g(r)$ obtained from our simulation. Since there is excluded volume interaction, there is a strong likelihood that a first neighbor shell will be found around $r = \sigma$. Hence the first

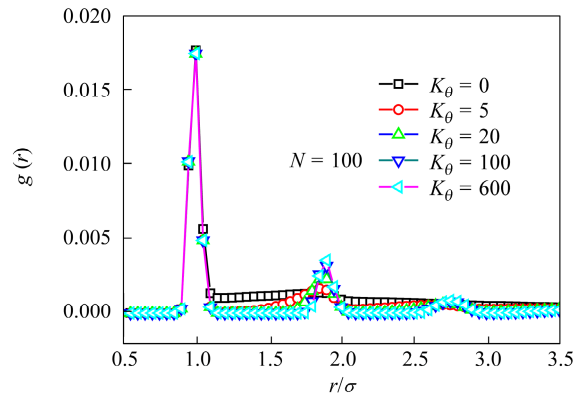


Fig. 4 The pair correlation function $g(r)$ for $N = 100$ under various K_θ values

peak appeared. The second peak corresponds to the most probable location for the next neighbors. As is shown in Fig. 4, with the increase of K_θ , the probability of finding a monomer located between the first and second peaks gradually decrease. And, as expected, all curves superimpose for $K_\theta > 100$ (results with $K_\theta = 200, 300, 400$ and 500 not shown for clarity).

Static structure factor $S(q)$ is the Fourier transform of $g(r)$. This function is particularly interesting since it can be measured experimentally by light scattering, small-angle X-ray scattering, *etc.* In Fig. 5 we plot $S(q)$ for $K_\theta = 0, 5, 20$ and 100 respectively, for various N in each case. We indeed observed, for each K_θ , a N -independent behavior of $S(q)$ in the range of $2.5/R_g \leq q \leq \pi/l$, where l is the average bond length, $l \approx 0.97$ in our simulations. For flexible chains with only excluded volume effects, scaling arguments predict that the static structure factor $S(q)$ should obey a power law function $q^{-1/\nu}$ in the range $2.5/R_g \leq q \leq \pi/l$. According to the above-mentioned range, we use power law $y = ax^b$ to fit the static structure factor $S(q)$. It is indeed observed (Fig. 6) and yields $\nu = 0.609 \pm 0.002$ for $N = 100$ and $K_\theta = 0$. Our result is in fair agreement with the theoretical estimate *i.e.* $\nu = 0.588$ for chain with excluded volume interactions. But when K_θ is large, for example $K_\theta = 100$, by fitting the N -independent part of $S(q)$ with a power law function, we obtained $S(q)$ like $q^{-1/\nu}$ with $\nu = 0.953 \pm 0.004$. If the chain is rod-like, $S(q)$ is like q^{-1} . Figure 6 reveals that if K_θ is large enough, we are close to the rod-like behavior of $S(q)$, for this range of q values. This has also been observed in a recent simulation of worm-like chains^[5].

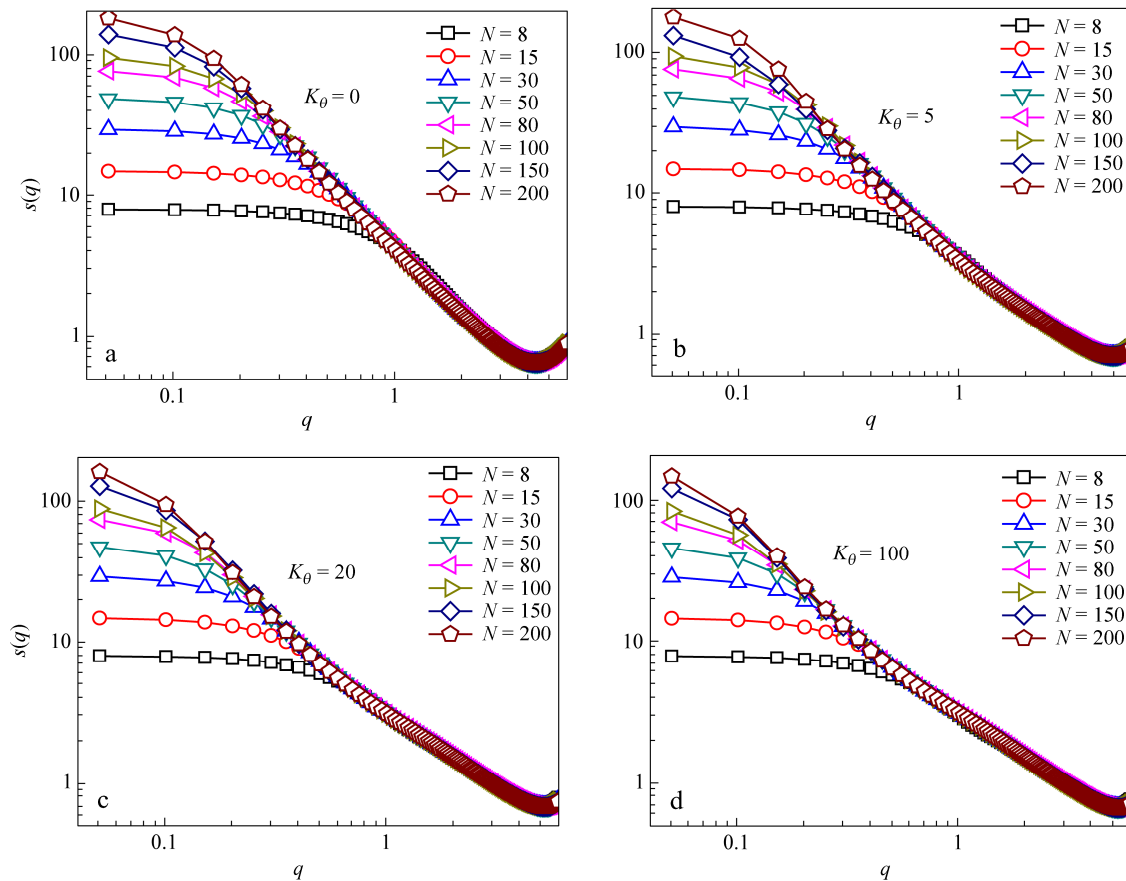


Fig. 5 Static structure factor $S(q)$ for different chain lengths N and different K_θ values

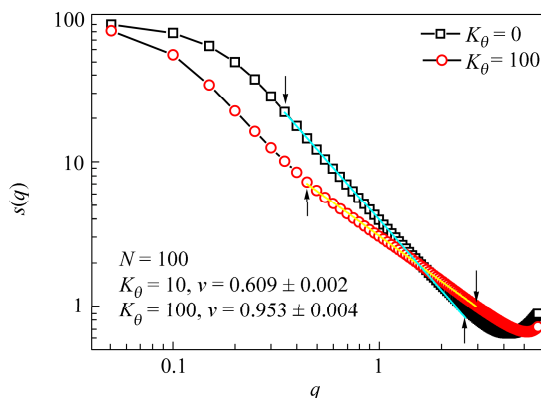


Fig. 6 Static structure factor $S(q)$ and its fitted curves for $N = 100$ and $K_\theta = 0$ and 100 respectively

$S(q)$ is fitted with power law function $y = ax^b$ in the range of $2.5/R_g \leq q \leq \pi/l$, which are marked by arrow pairs.

CONCLUSIONS

We have investigated the influence of the chain stiffness on the scaling laws for polymers in dilute good solutions using Langevin dynamics simulations with a bead-spring model whose potential energy was the sum of WCA and FENE potential or WCA, FENE and bending potential. Compared to flexible chains with only excluded volume interactions, chain stiffness only influences the prefactors of R_0 , τ_r and D . Our results reproduce well the scaling behavior predicted by Rouse theory in good solvents. Because scaling exponents in scaling laws which we examined reflect global properties, and prefactor reflects microscopic structure of chain, our results, based on chains with $l < l_p < 7l$ and $N \leq 200$, indicate that chain stiffness only influences the microscopic structure of polymer chains, but does not drastically influence the scaling of global dynamic properties of polymer chains. Our study of the static properties shows that $g(r)$ and $S(q)$ are very sensitive to the chain stiffness. And the scaling behavior of $S(q)$ is indeed changed from flexible chain characteristics to rod-like ones (for $2.5/R_g < q < \pi/l$) when the bending force constant is fairly large.

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