Crossover between Linear and Nonlinear Elastic Behaviors in Random and Self-Avoiding Walks

Satoru Masatsuji, Natsuko Nakagawa, and Kaoru Ohno*

Department of Physics, Yokohama National University, 79-5 Tokiwadai, Hodogaya, Yokohama 240-8501, Japan

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ABSTRACT: In order to reexamine earlier studies on the elastic behavior of a single-chain molecule precisely, we performed a large-scale Monte Carlo simulation of a random walk (RW) and a self-avoiding walk (SAW) on a simple cubic lattice with lattice constant a under an external force X in the x direction. We use the important-sampling enrichment algorithm generating 1 000 000 samples of chain length N up to 300. We first confirmed that the mean stretching distance behaves exactly as $\langle x_N\rangle_{\mathrm{RW}} = Na(e^{\beta Xa} - e^{-\beta Xa})/(e^{\beta Xa} + e^{-\beta Xa} + 4)$ for RW ($\beta = 1/k_BT$) and as $\langle x_N\rangle_{\mathrm{SAW}} \sim$ const $\times N^{2\nu}\beta Xa$ (for very small X) and $\sim$const $\times X^{2/3}$ (for $0 \ll X \ll k_BT/a$) for SAW in accordance with the scaling theory by de Gennes (*Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979) and Pincus (*Macromolecules* **1976**, *9*, 386). However, for SAW, the crossover between these two behaviors is rather smooth in contrast to the earlier Monte Carlo result by Webman et al. (*Phys. Rev. A* **1981**, *23*, 316) showing an abrupt transition. The present study resolves the long-standing difficulty concerning if the crossover is abrupt or smooth, which has been raised by Oono et al. (*Macromolecules* **1981**, *14*, 880) in their renormalization-group study. The crossover point $\eta_c = \beta X_c R_0$ is accurately determined in the present study. On the other hand, we found that the relation $\langle x_N\rangle \sim R_0^2X/3k_BT$ holds up to the proportional constant for very small X irrespectively for SAW and RW, or for any real chains (R_0^2 is the mean-square end-to-end distance at $X = 0$), as first suggested by Webman et al. and reconfirmed by Oono et al.

I. Introduction

The theory of rubber elasticity has been established since long ago in connection with entropic properties of chain molecules.[1–3] Recently, precise experiments on the elastic behavior of a single polymer chain have become possible by means of the atomic force microscopy (AFM).[4–8] In addition, various numerical studies on the elastic behavior of polymer networks, semiflexible chains, or a single polymer below Θ point have appeared recently.[9–12] In these circumstances, however, the theoretical study on the crossover between linear and nonlinear elastic behaviors of a single-chain molecule has not progressed since the early 1980s[13–16] with leaving an unsolved problem whether the crossover is smooth or not. Here we again focus on this issue. Using the scaling theory of a flexible polymer chain composed of N segments of length a under a stretching force X at the temperature T, de Gennes[13] and Pincus[14] predicted the stretching $\langle x_N\rangle$ behaving as

$$\langle x_N\rangle \sim \mathrm{const} \times N^{2\nu}\beta Xa, \quad \text{for } X \sim 0 \tag{1}$$

($\nu = 0.59$ is the exponent for the gyration radius) and

$$\langle x_N\rangle \sim \mathrm{const} \times X^{2/3}, \quad \text{for } 0 \ll X \ll k_BT/a \tag{2}$$

Equations 1 and 2 describe respectively the elastic behaviors in very weak and medium stretching regimes. The crossover behavior in the intermediate regime was studied by means of a Monte Carlo simulation using Lennard-Jones potential (for a flexible chain with N = 10, 20, 40, and 80)[15] or the field-theoretical renormalization-group approach.[16] While the Monte Carlo result[15] suggests a rather abrupt transition from the linear behavior to the 2/3 power-law behavior in X, the renormalization-group result[16] suggests a rather smooth transition. This contradiction has been a long-standing problem unsolved until now.

By means of a computer simulation of a self-avoiding walk (SAW) on a lattice, accurate analysis and comparison with a random walk (RW) are possible,[17] and it is a straightforward application to study these linear and nonlinear elastic behaviors of a SAW. Nevertheless, to our knowledge, there has been no such study, and the investigation of the most fundamental part of the elastic behaviors of a SAW has not progressed since the early 1980s.

The purpose of the present paper is to carry out a large-scale importance-sampling Monte Carlo simulation of a SAW under a tensile force to analyze its linear and nonlinear elastic behaviors accurately. We use the enrichment algorithm to generate a lot of SAW samples simultaneously. We generate 1 000 000 samples of SAW with up to $N = 300$ segments, which should be compared with the previous Monte Carlo simulation for a chains with N = 10, 20, 40, and 80 segments.[15]

II. Exact Theory

A. General Walks. We start from the general theory of a chain on a lattice under a tensile force. Each configuration of a chain is called a walk. Here we consider the simplest case of a simple cubic lattice only. For any walks starting $x = x_0 = 0$ and ending at $x = x_N$ by N steps under a force X acting on the x direction, the partition function is given by

$$\begin{aligned} Z &= \sum_{\text{walks}} x_N \exp(\beta X x_N) = \sum_{\text{walks}} x_N \exp\left[\beta X \sum_{i=1}^{N} (x_i - x_{i-1})\right] \\ &= \sum_{\text{walks}} \prod_{i=1}^{N} \exp\left[\beta X \sum_{i=1}^{N} (x_i - x_{i-1})\right] \end{aligned} \tag{3}$$

where $\beta = 1/k_BT$ and the summation runs over all possible walks. For very small values of X, Webman et al. argued that the equation

$$\langle x_N\rangle \sim \frac{1}{3}\beta X R_0^{\,2} \tag{4}$$

holds up to the proportional constant for any real chain, where R_0^2 is its mean-square end-to-end distance in the absence of the external force, and confirmed it by their Monte Carlo

* Corresponding author. E-mail: ohno@ynu.ac.jp.

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simulation.[15] This relation is, however, obvious as demonstrated by Oono et al.[16] because the small X behavior of $\langle x_N \rangle$ can be readily calculated by expanding the Boltzmann weight in the summation over all walks which distribute spherically symmetric in the absence of the external force X: $\langle x_N^2 \rangle = \langle y_N^2 \rangle = \langle z_N^2 \rangle = \langle r_N^2 \rangle/3$. That is, we should have

$$\langle x_N \rangle = \frac{\sum_{\text{walks}} x_N \exp(\beta X x_N)}{\sum_{\text{walks}} \exp(\beta X x_N)} \xrightarrow[x \to 0]{} \beta X \frac{\sum_{\text{walks}} x_N^2}{\sum_{\text{walks}} 1}$$
$$= \beta X \langle x_N^2 \rangle = \frac{1}{3} \beta X \langle r_N^2 \rangle = \frac{1}{3} \beta X R_0^2 \quad (5)$$

as a general identity.

B. RW. In particular, for random walks, it becomes

$$Z_{\text{RW}} = \prod_{i=1}^{N} (e^{\beta X a} + e^{-\beta X a} + 4) = (e^{\beta X a} + e^{-\beta X a} + 4)^N \quad (6)$$

where a is a length of one segment. Therefore, we have

$$\langle x_N \rangle_{\text{RW}} = \frac{\partial}{\partial(\beta X)} \log Z_{\text{RW}} = \frac{Na(e^{\beta X a} - e^{-\beta X a})}{e^{\beta X a} + e^{-\beta X a} + 4} \quad (7)$$

For very small X, it becomes

$$\langle x_N \rangle \approx \frac{1}{3} \beta X N a^2 \quad (8)$$

For the mean-square end-to-end distance in the x direction, we have

$$\langle x_N^2 \rangle_{\text{RW}} = \frac{\partial^2}{\partial(\beta X)^2} \log Z_{\text{RW}} = \frac{Na^2(e^{\beta X a} + e^{-\beta X a})}{e^{\beta X a} + e^{-\beta X a} + 4} - \frac{Na^2(e^{\beta X a} - e^{-\beta X a})^2}{(e^{\beta X a} + e^{-\beta X a} + 4)^2} \quad (9)$$

which behaves in the limit $X \to 0$ as

$$\lim_{x \to 0} \langle x_N^2 \rangle_{\text{RW}} \approx \frac{1}{3} N a^2 \quad (10)$$

Therefore, adding three directions (note that the same form holds for the y- and z-directions), we have

$$R_{0,\text{RW}}^2 = \langle r_N^2 \rangle_{\text{RW}} = N a^2 \quad (11)$$

for the mean-square end-to-end distance in the absence of the external field. Using eq 11, eq 8 can be rewritten as

$$\langle x_N \rangle_{\text{RW}} \approx \frac{1}{3} \beta X R_{0,\text{RW}}^2 \quad (12)$$

which is a special case of eq 4.

III. Importance-Sampling Enrichment Algorithm

The simple sampling Monte Carlo simulation is not suitable for the present purpose. This is because, under the existence of a strong external force X, while the walks stretched out in the x-direction, such samples are not chosen in the process of Monte Carlo sampling with the probability very close to one. An alternative approach is to use the biased sampling Monte Carlo sampling as follows. According to eq 3, when we elongate the length of a chain one by one, the direction of each elongated segment is weighted with the probability proportional to $\exp[\beta X(x_i - x_{i-1})]$. That is, we sample the walk trajectories by elongating segments one by one with a Boltzmann weight

$$\frac{\exp[\beta X(x_i - x_{i-1})]}{e^{\beta X a} + e^{-\beta X a} + 4} \quad (13)$$

where the denominator is required for the normalization of the probability. In the case of RW, all six directions of elongation toward nearest neighbors are allowed with this probability. On the other hand, for SAW, the direction of elongation violating self-avoiding condition is not allowed and simply discarded.

In the present study, we use the enrichment algorithm to elongate segments. In the enrichment algorithm for a self-avoiding walk, we generate chains with chain length $n + 1$ from those with chain length n which is shorter by one segment, using a standard Monte Carlo technique.[18–21] On a simple cubic lattice, we have five ways of elongating one end of a chain by one segment because the sixth direction makes the chain fold backward on itself. For very long chains, the success ratio is asymptotically given by $\mu/5 = 0.937\,06$ (the effective coordination number of the simple cubic lattice is $\mu = 4.6853$[22]) when $X = 0$. Then, one-step longer chains are generated. At each step, the self-avoiding condition is tested; unless this condition is fulfilled, generated configurations are simply discarded.

If we would consider all possible realizations at the $n + 1$st step from M_n distinct realizations at the nth step, we have to make all $5M_n$ trials. However, doing only mM_n trials ($m < 5$), which are much less than the full $5M_n$ trials, we can collect enough number of samples which are statistically isomorphic to the full realizations. That is, we generate only a limited number of samples M_{n+1} from M_n samples by a Monte Carlo method. This process can be iterated when $M_n \sim M_{n+1} \sim \ldots$. The condition $M_{n+1}/M_n \sim 1$ is satisfied when we choose $m > 5/\mu = 1.0672$. In practice, it is necessary to increase M_n gradually as n increases because one has to avoid an unphysical "bias" caused from this iteration. (For small n, it is better to work with somewhat larger values of m.) This enrichment algorithm significantly reduces computing time, since it becomes quite efficient asymptotically for very long chains. In this way, we create 1 000 000 samples of SAW chains whose length N is equal to 100, 200, and 300 under various strengths of the external stretching force X.

Table 1. Calculated Mean-Square End-to-End Distance $\langle r^2 \rangle$ and Its Square Root R_0 for RW and SAW for Various Chain Length N

	N	$\langle r^2 \rangle$	R_0
RW	100	99.253	9.963
	200	198.523	14.090
	300	296.210	17.211
SAW	20	38.716	6.222
	30	62.494	7.905
	50	116.817	10.808
	70	172.684	13.141
	100	264.987	16.278
	150	431.782	20.779
	200	605.923	24.616
	250	815.149	28.551
	300	975.436	31.232

IV. Results

First of all, we focus on RW. The mean-square end-to-end distance, $\langle r^2 \rangle_{\text{RW}}$ (and its square root, $R_{0,\text{RW}}$), obtained by the simulation in the absence of the external force are listed in units of the segment length a in the upper part of Table 1. From this table, we find that the relation $R_{0,\text{RW}} = Na^2$ (eq 11) holds accurately within the error of 1%. When one switch on the force, the resulting force–distance dependence in the case of RW is shown in Figure 1 by open circles for the chain lengths (a) $N = 100$, (b) $N = 200$, and (c) $N = 300$. In this figure, the abscissa is $\beta X a$, and the ordinate is the stretching distance $\langle x_N \rangle$ measured in units of the segment distance a. The lower solid curve connecting open circles in this figure denotes the theoretical curve given by eq 7. As clearly seen, the simulation and the theory agree quite well, which indicates the validity of the present treatment of the external force in the biased Monte Carlo

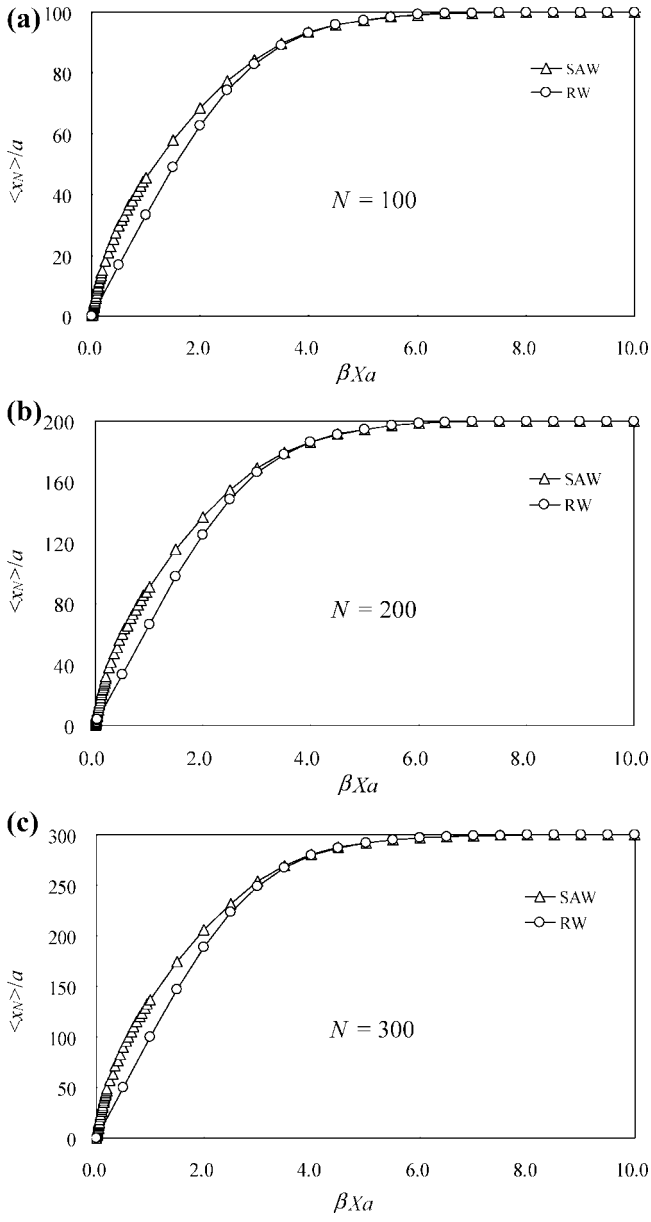

Figure 1. Force–distance curves of random (circles) and self-avoiding (triangles) walks with the chain length (a) $N = 100$, (b) $N = 200$, and (c) $N = 300$. The theoretical curve for the random walk is also depicted with a solid line (the lower curve).

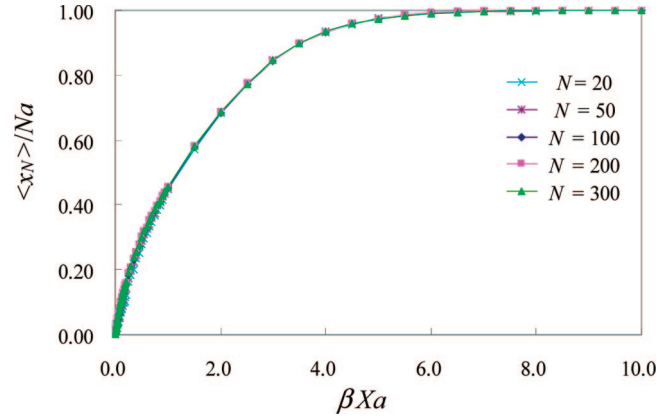

Figure 2. Force–distance curves of self-avoiding walks with the chain length $N = 20$, 50, 100, 200, and 300. In the ordinate, the stretching distance $\langle x_N \rangle$ is normalized by the chain length Na.

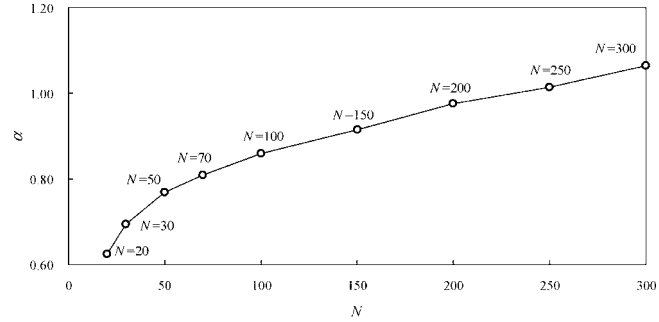

Figure 3. Initial slope α in the force–distance curve (Figure 2) vs chain length N.

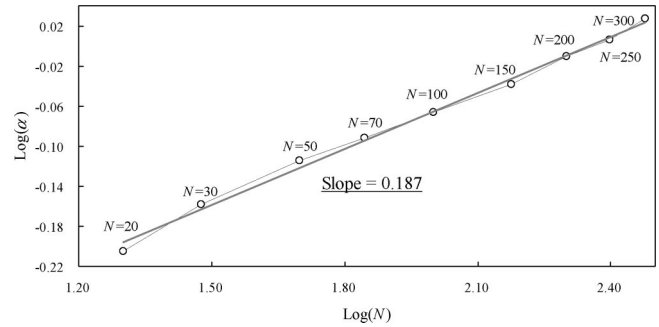

Figure 4. Double-logarithmic plot of Figure 3.

sampling and also the accuracy of the present simulation. The initial slope is of course $N/3$, in agreement with eq 8.

Next, we turn our attention to SAW. The resulting force–distance dependence for SAW is shown by open triangles in the same Figure 1. Comparing the results of RW and SAW, we find that the initial slope α and the mean distance itself of SAW are much larger than those of RW, indicating that the self-avoiding effect is quite large. These force–distance curves for SAW with $N = 100$, 200, and 300 together with the curves with shorter $N = 20$ and 50 are all superposed in Figure 2, where the normalized distance $\langle x_N \rangle / Na$ is plotted versus βXa. As seen in this figure, the overall behavior is quite similar to each other for all chain lengths, while a very slight deviation appears in the small βXa region. The initial slope, i.e., the elastic constant, $\lim_{x \to 0} \partial \langle x_N \rangle / \partial X$ divided by $Na^2\beta$ of all these curves, is plotted versus the chain length N in Figure 3. Obviously, the values are much larger than $1/3 = 0.33$ of RW as indicated already above. More importantly, the initial slope is N-dependent; i.e., the elastic constant is nonlinear in N, reflecting that the effect of the strain propagates not only through the bonds but also through the interconnection between distant segments.[13] The double-logarithmic plot of this curve is shown in Figure 4. From this figure, we find

$$\lim_{X \to 0} \frac{\partial \langle x_N \rangle}{\partial X} \propto N^{1.187} \tag{14}$$

The exponent expected from the scaling theory (1) is $2\nu = 1.18$, and the agreement is fairly good.

When the strength of the force increases, the force–distance curve becomes nonlinear, and finally the distance saturates and approaches the chain length. To see the nonlinear behavior in the medium force regime in detail, we replot the force–distance curves in double-logarithmic scale in parts a, b, and c of Figure 5 for the chain lengths $N = 100$, 200, and 300, respectively. While the slope is almost unity for small values of the force as expected in the linear behavior, it becomes almost equal to 2/3 for larger values of the force as expected from the scaling theory, eq 2. The crossover in between occurs rather smoothly in

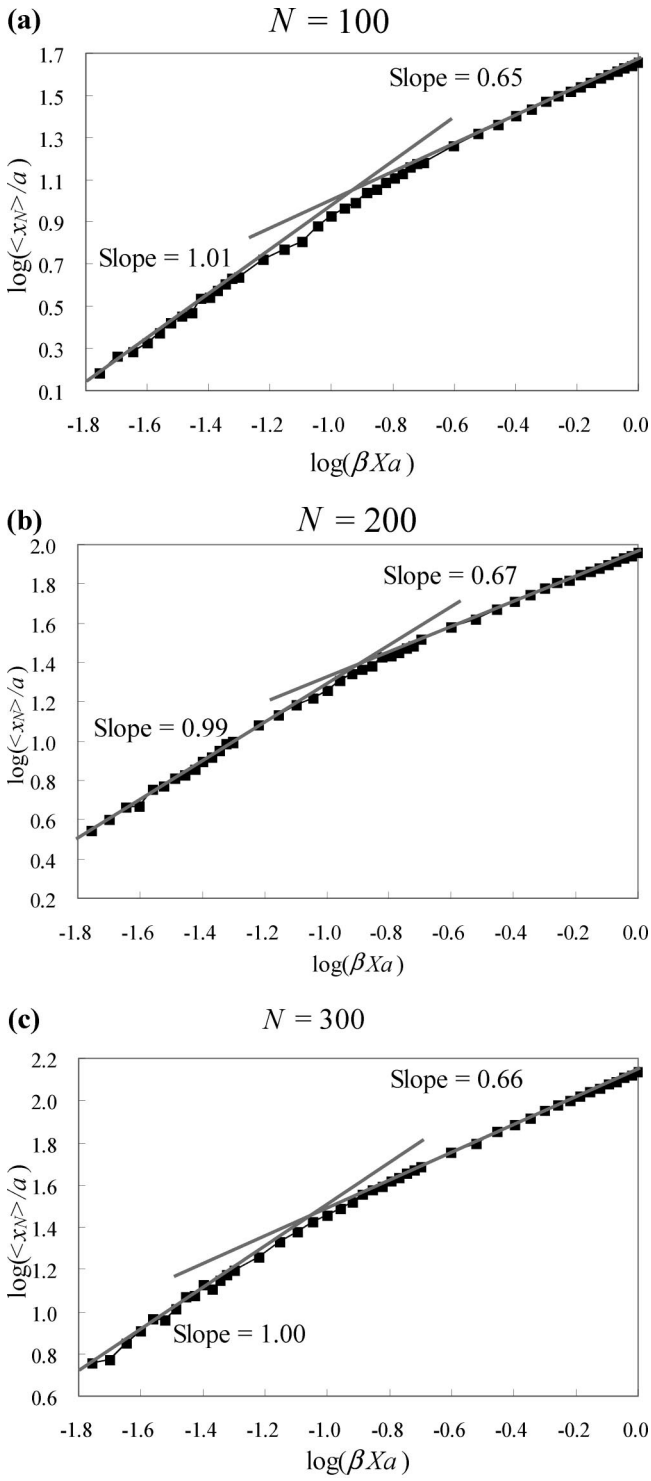

Figure 5. Double-logarithmic plots of the force–distance curves of the SAW with the chain length (a) $N = 100$, (b) $N = 200$, and (c) $N = 300$.

Table 2. Crossover Point $\beta X_c a$ and the Corresponding $\eta_c = \beta X_c R_0$ for $N = 100$, 200, and 300

N	$\langle r^2 \rangle$	R_0	$\log(\beta X_c a)$	$\beta X_c a$	$\eta_c = \beta X_c R_0$
100	264.987	16.278	−0.825	0.150	2.44
200	605.923	24.616	−0.971	0.107	2.63
300	975.436	31.232	−1.041	0.091	2.84

contrast to the earlier Monte Carlo result showing an abrupt transition (Figure 2 of ref 15). Our result is rather similar to the result of the renormalization-group theory (Figure 2 of ref 16). This result resolves the long standing difficulty concerning

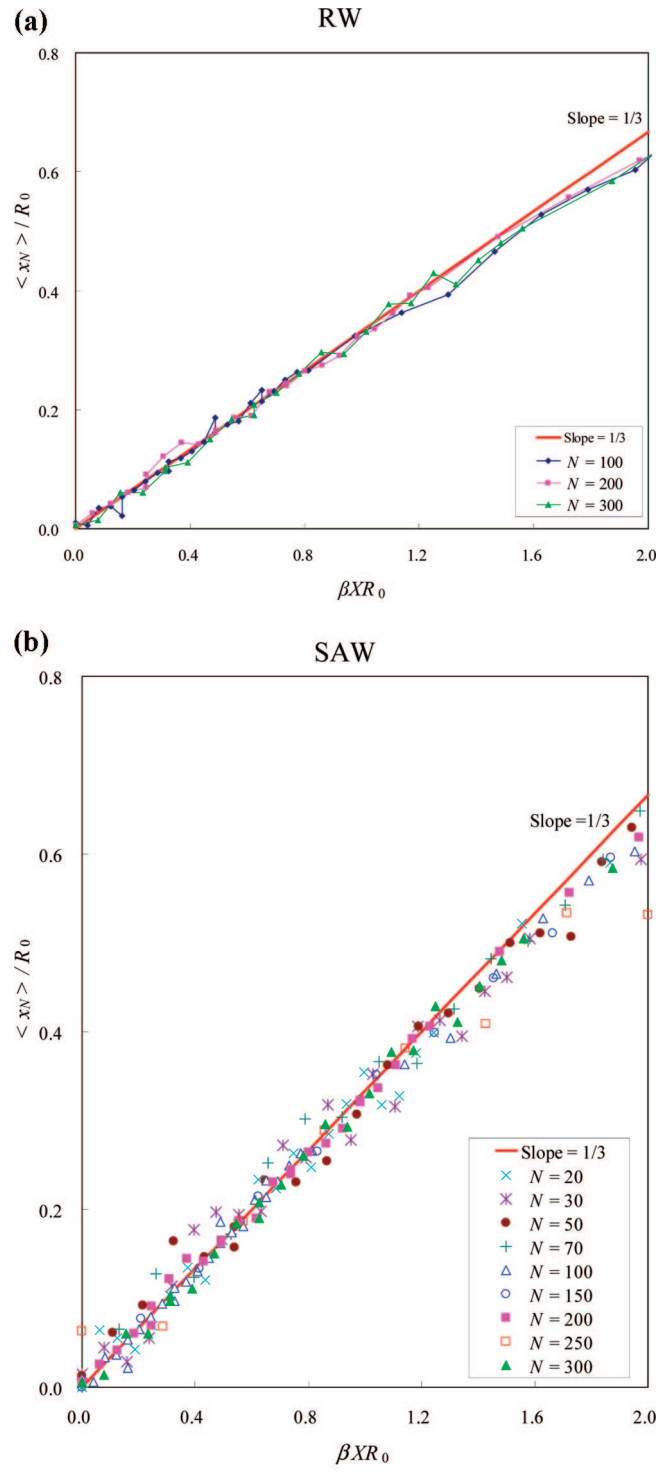

Figure 6. Force–distance curve with the scaling variables, $\langle x_N \rangle / R_0$ vs $\beta R_0 X$, for (a) RW and (b) SAW. The initial slope coincides with 1/3 as expected in eq 4.

if the crossover is abrupt or smooth, which has been raised by Oono et al. in their renormalization-group study.[16] The crossover point, $\beta X_c a$, can be identified from Figure 5 and listed in Table 2 together with the corresponding value for $\eta_c = \beta X_c R_0$ for the chain length $N = 100$, 200, and 300. (The value of R_0 in Table 1 is used to get this η_c.) The resulting value for $\eta_c = \beta X_c R_0$ is 2.44 for $N = 100$ and weakly increases with N. It becomes 2.84 for $N = 300$. This behavior seems reasonable, but it is interesting to note that this behavior is completely different from the behavior expected from the renormalization-group theory, which tells $\eta_c \sim 1$ irrespective for N.[16] This is simply because the

renormalization-group theory cannot predict the absolute value for η_c.

Finally, in order to check that the relation 4 holds irrespectively for RW and SAW, we use the result of the mean square end-to-end distance, $\langle r^2 \rangle$ (and its square root, R_0), in the absence of the external force, which are listed in the lower part of Table 1. Redrawing the force–distance curve with the scaling variables, $\langle x_N \rangle / R_0$ vs $\beta X R_0$, we obtain parts a and b of Figure 6 for RW and SAW, respectively. From these figures, we find that the initial slope is accurately equal to 1/3 irrespective for RW and SAW for any chain lengths N, suggesting that relation 4 holds for any walks. This might seem a surprising result because the amplitude itself is not usually universal, but according to eq 5, this relation is exact for any walks because of the spherical symmetry of the end-to-end distribution function.

V. Concluding Remarks

In this paper, we focused again on the elastic behavior of a single-chain molecule theoretically. We have carried out large-scale Monte Carlo simulation of RW and SAW under the tensile force by means of the enrichment algorithm generating 1 000 000 samples of chain length N up to $N = 300$. For RW, our result fully coincides with the theoretical curve, which suggests the accuracy of the present simulation. For SAW, we have confirmed the scaling laws (1) and (2) are satisfied, and that the crossover between the linear and nonlinear elastic behaviors is smooth in accordance with the renormalization-group result by Oono et al.[16] The present study resolves the long-standing problem concerning the crossover behavior. The crossover point $\eta_c = \beta X_c R_0$ was accurately determined in the present study. We confirmed also that the relation $\langle x_N \rangle \sim R_0^2 X / 3 k_B T$ holds irrespectively for SAW and RW, where R_0^2 is the mean-square end-to-end distance at $X = 0$. In our future work, we are planning to extend the present analysis to star polymer systems to consider more realistic rubber elasticity.

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