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Monte Carlo calculation of second and third virial coefficients of small-scale comb polymers on lattice

Kazuhiro Shida

Tohoku University Biomedical Engineering Research Organization (TUBERO), Sendai 980-8575, Japan

Atsuo Kasuya

Center for Interdisciplinary Research, Tohoku University, Sendai 980-8578, Japan

Kaoru Ohno

Department of Physics, Graduate School of Engineering, Yokohama National University, Yokohama 240-8501, Japan

Yoshiyuki Kawazoe

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Yo Nakamura

Department of Macromolecular Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

(Received 15 November 2006; accepted 2 March 2007; published online 17 April 2007)

This paper reports the first computational estimation of the comb polymers' third virial coefficients. The number of the chains in the comb polymers range from 5 to 11. An algorithm that counts the contributing terms of the third virial coefficients in an accelerated manner is presented along with its efficiency dependence on the polymers' size. In addition, the second virial coefficients are estimated for the comb polymers and compared to previously reported results. © 2007 American Institute of Physics. [DOI: [10.1063/1.2720380](https://doi.org/10.1063/1.2720380)]

I. INTRODUCTION

Comb polymers have a main chain and many side chains that branch off at numerous points along the main chain. Such a molecule design is interesting because many properties of polymers can be modified by the existence of the branches.¹ Moreover, precise control of the number, connection topology, and length of individual chains in a comb polymer has become available recently.^{2,3} Such progress in experimental technology attracts our attention to simulations of the corresponding systems.

One notable and very complicated example is the excluded volume effect (EVE) of comb polymers. The EVE between side chains appears in various forms of change in the configurational properties of the polymers and has been studied in many previous papers involving computer simulations of various types.^{4–11} However, no research on virial coefficients of comb polymers has been reported so far, in spite of the great interest in second and third virial coefficients of polymeric solutions. This paper presents a computational estimation of second and third virial coefficients of small-scale combs. To the author's knowledge, this report is the first to describe this subject.

The n th virial coefficient A_n is defined by a virial expansion

$$\frac{\Pi}{N_A k_B T} = \frac{c}{M} + A_2 c^2 + A_3 c^3 + \cdots, \quad (1)$$

where Π is the osmotic pressure of the system. In Eq. (1), N_A is Avogadro's number, c the mass concentration of the polymer chain, and M the molecular weight of the polymer chain,

which is identical to the number of segments in a polymer when a lattice model is used.

A straightforward method of calculation, assuming a lattice model and a hard-core potential, was used by Bruns¹² to estimate the virial coefficients of the lattice polymers. However, this approach resulted in a severe limitation on the scale of the simulation. The only study that has devoted sufficient attention to the efficiency of such calculations was presented by Poland,¹³ who used the symmetry of sample lattice chains to simplify the calculation. Poland showed that such a calculation is effective for up to seven segments per chain. However, the improvement of efficiency that is provided by Poland's simplification remains insufficient if one wants to perform such a calculation on the comb polymers, which have multiple chains connected together, each with more than ten segments.

Off-lattice simulations might be a more natural approach to estimate virial coefficients. That is to say, the n th virial coefficient of polymer molecules can be estimated using multidimensional integration over the positions of n different molecules and the internal configuration of polymer molecules. Once an ensemble of polymer configurations is available, no fundamental difficulties remain to prevent an evaluation of these multidimensional integrals.

This approach has been taken by Vega and MacDowell¹⁴ and Rubio *et al.*¹⁵ A salient disadvantage of this approach is that reduction of the sampling point in the multidimensional space is almost the only way to reduce the computational burden of the multidimensional integrals. We use a lattice model (simple cubic) because a larger possibility exists to

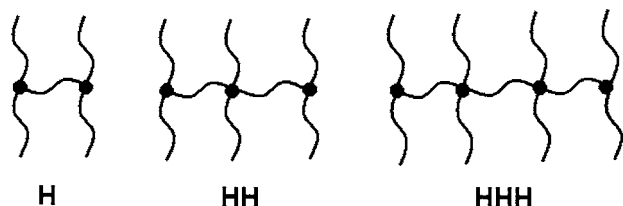


FIG. 1. These comb polymers are simulated in a lattice model. Their second and third virial coefficients are estimated.

explore the counting algorithm of the interfering configuration between chains than the possibility presented by off-lattice multidimensional integrals.

In the next section, the algorithms we developed and used are introduced. Then, in the final section, the results are presented for small-scale comb polymers called H, HH, and HHH (see Fig. 1), whose numbers of chains f range from 5 to 11. It is assumed that the chain lengths are all the same in a comb. These polymers can be regarded as the simplest examples in an infinitely long series of (regularly branched) comb polymers.

II. METHOD

An estimation of virial coefficients of the comb polymers requires us to solve two computationally heavy problems. The first problem is the sample generation of lattice comb polymers. The segments have a large probability of collision near the branch points. The comb polymers have multiple branch points. Therefore, the efficiency of sample generation is strongly affected. We developed a fast lattice-chain-generation algorithm and regained the efficiency, even in the case of comb polymers. The algorithm details are introduced elsewhere.¹⁶

The second problem is the large computational burden of estimation of the virial coefficients. Estimation formulas of virial coefficients, which take intermolecular potential as input, can be derived through the cluster integral theory. Here, we briefly introduce the basic formulas, then proceed to elucidate the details of the proposed acceleration method.

The magnitude of the n th virial coefficient is related to the strength of interaction among n molecules. Usually, the interaction is described as a combination of two-body interactions. The estimation formula for the second virial coefficient can be written as an integral over positions of two molecules, \mathbf{r}_1 and \mathbf{r}_2 ,

$$A_2 = -\frac{N_A}{2VM^2} \int \int (\exp^{-U(r_{12})/kT} - 1) d\mathbf{r}_1 d\mathbf{r}_2. \quad (2)$$

Therein, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between molecule i and molecule j , and $U(r_{ij})$ is the intermolecular potential function. The value V is the system volume.

Likewise, the integration formula for the third virial coefficient involves the positions of three molecules \mathbf{r}_1 , \mathbf{r}_2 , and \mathbf{r}_3 ,

$$A_3 = -\frac{N_A^2}{3VM^3} \int \int \int (\exp^{-U(r_{12})/kT} - 1)(\exp^{-U(r_{23})/kT} - 1) \times (\exp^{-U(r_{31})/kT} - 1) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3. \quad (3)$$

The V can be canceled out by the translational degree of freedom. Integrations should be transformed appropriately into summations in the cases of discretized models.

Flexible polymer molecules have no fixed shape. Consequently, the virial coefficients are dependent on the nature of the constantly changing shape of the polymer molecules. As a suitable model for such a subject, we have been using a Monte Carlo sampled simple cubic lattice model.¹⁷ In this model, each polymer chain is a self-avoiding random walk on the lattice. The position of each polymer segment is discretized. Moreover, segment-segment interaction is assumed to be a hard-core potential such as

$$u(r) = \begin{cases} 0 & \text{for } r \neq 0 \\ \infty & \text{for } r = 0, \end{cases} \quad (4)$$

which prevents the segments from mutually overlapping. A sampled polymer molecule in the model is described as

$$\mathbf{r}_{i,1}, \mathbf{r}_{i,2}, \mathbf{r}_{i,3}, \dots, \mathbf{r}_{i,M}, \quad (5)$$

where M is the number of the segments in each molecule, and i the index of the molecule in the system. Usually, complete monodispersity is assumed. For that reason, M is the same for all polymer molecules. The position of the polymer molecule is represented by the position of the first segment of the molecule, $\mathbf{r}_{i,1}$. As a result of these assumptions, the interactions between such molecules are summarized to give the following rule:

$$1 - \exp(-\beta U(r)) = 1 - \exp\left(-\beta \sum_{i,j(i>j)} u(r_{ij})\right) = \begin{cases} 1 & \text{when there is a collision} \\ 0 & \text{otherwise.} \end{cases} \quad (6)$$

Note that the information on the segment-segment connection along the polymer chains is not used in Eq. (6). Therefore, the formulas explained here are applicable for polymers with any connection topologies including the comb polymers. Similarly, the algorithm we will introduce obviates the use of the connection information; it is also applicable for the comb polymers.

Several such polymer molecules or chains are generated according to pseudorandom numbers. They form an ensemble of a system. The integrals already introduced in Eqs. (2) and (3) should be evaluated for a large number of such samples. Then, the virial coefficients are obtained as the sample average of such integrals, i.e., the average over the shapes.

A straightforward method of evaluating such integrals is to generate three chains, designated as chains 1, 2, and 3. The integration/summation for A_2 is performed for each of the three pairs of chains: chains 1-2, 2-3, and 3-1. Then, integration/summation for A_3 is performed on all three chains in the sample.

Assumptions of the lattice model and the step-function potential represented by Eq. (6) enable us to evaluate the integral in Eq. (2) by counting the number of unique segment-segment displacement vectors,

$$\mathbf{V}_{ijnm} = \mathbf{r}_{i,n} - \mathbf{r}_{j,m}. \quad (7)$$

This can be done because the integrand in the equation gives unity if two chains overlap at least at one point. Apparently, counting segment-segment displacement vectors and filtering nonunique vectors require $\sim O(M^2)$ of computational complexity: there are up to M^2 unique ways to place a pair of chains such that they interact.

The integrand for the third virial coefficient is contributed by each combination of three segment-segment displacement vectors, which corresponds to a situation of three chains touching each other. This means that the contributing three segment-segment displacement vectors should satisfy the following equation:

$$\mathbf{V}_{12nm} + \mathbf{V}_{23st} + \mathbf{V}_{31uv} = 0. \quad (8)$$

Scanning all these indices requires $\sim O(M^6)$ of computational complexity. At this point, the problem becomes very challenging in terms of computing: there are as many as M^6 combinations to place three chains such that they have a mutual and simultaneous interaction, and we must count the exact number of unique combinations. Irrespective of the performance of the computer used for the simulation, $O(M^6)$ soon becomes an intractable burden because the value of M must be sufficiently large to achieve reliable results in the scaling region. On the other hand, it is established¹² that the value of A_3 behaves as $\sim M^{0.528}$ for linear polymers. The actual number of the contributing term is expected to grow far more slowly than $O(M^6)$ (because $A_3 M^3 \sim M^{3.528}$), suggesting the possibility of more efficient methods to realize the summation.

We arrived at the conclusion that a sophisticated algorithm was necessary before further study of this subject could be pursued properly. Therefore, we tested several algorithms, including hash searching and complicated clustering of the displacement vectors. We discovered that the following algorithm is quite simple and effective, at least in the case of linear and star polymers.¹⁸

The algorithm focuses on the more difficult problem, namely, the A_3 counting. The $\sim O(M^6)$ combinations can be reduced by performing the checking in a two-stage manner. The key of the two-stage idea is that only a minority of all possible combinations satisfies Eq. (8) (especially for large M). Hence, when combinations are separated into groups of appropriate average size, q , many groups will have no contribution to the integral. If the filtering of such groups is performed at the first stage of checking, the number of overall processing steps will be reduced even if all q combinations are checked at the second stage for each remaining group. Because the filtering must be performed at a reasonable computing cost, the following procedure is suggested.

In the algorithm, the displacement vectors are grouped; consequently, the grouping of the combinations is realized as a direct product of the displacement vector groups. A representative displacement vector is definable for each group

such that the distance between the representative and each member vector is always less than d . In other words, each segment-segment displacement vector \mathbf{V} is decomposed into a representative vector $\mathbf{R}(\mathbf{V})$ and a residual or an error vector \mathbf{e} , such as $\mathbf{V} = \mathbf{R}(\mathbf{V}) + \mathbf{e}(\mathbf{V})$ and $|\mathbf{e}(\mathbf{V})| < d$. Note that displacement vectors in a group share the same \mathbf{R} . For that reason, it is called representative.

A simple cubic subsection of the displacement vector space, taking the centers of the subsection cubes as the end points of the representative vectors, is a straightforward means of realizing such a grouping, under which one can assume that $d = (\sqrt{3}/2)N_c$, where N_c is the side of the subsection cubes. It is easy to see that the cost of computing $\mathbf{R}(\mathbf{V})$ is minimum.

The representative vectors can be substituted to Eq. (8) in place of the corresponding displacement vectors to obtain an approximated value of the left-hand side of Eq. (8). That is, the left-hand side of Eq. (8) turns out to be

$$\begin{aligned} &\mathbf{R}(\mathbf{V}_{12nm}) + \mathbf{R}(\mathbf{V}_{23st}) + \mathbf{R}(\mathbf{V}_{31uv}) \\ &+ \mathbf{e}(\mathbf{V}_{12nm}) + \mathbf{e}(\mathbf{V}_{23st}) + \mathbf{e}(\mathbf{V}_{31uv}). \end{aligned} \quad (9)$$

A condition for making Eq. (8) hold is that the vector sum of the first three terms of Eq. (9) should be pointing to somewhere within a $3d$ radius from the origin because none of the last three vectors can have a magnitude greater than d . This is a necessary condition that is shared by all displacement vectors in the current group. Therefore, a single evaluation of condition

$$|\mathbf{R}(\mathbf{V}_{12nm}) + \mathbf{R}(\mathbf{V}_{23st}) + \mathbf{R}(\mathbf{V}_{31uv})| < 3d \quad (10)$$

can determine whether there is a possibility of contribution to Eq. (3) in the current group of combinations or not. Equation (10) is useful in screening out the unnecessary combinations of indices effectively, before Eq. (8) is applied.

The result of the counting does not change from that of the original algorithm. In addition, we demonstrated this equivalence of the new algorithm with the conventional one through an exhaustive check of many sample chains in a previous paper.¹⁸

An important point to discuss is the degree to which the two-stage algorithm reduces the number of combinations. Two major factors pertain to this point. The value of the adjustable parameter of the algorithm, N_c , is the first one; we can find the best value in an empirical manner. The second factor is the distribution of contributing terms in the combination space. The distribution is very difficult to picture. Therefore, it is useful to discuss the worst possible case of the distribution. The algorithm needs $O(M^6/q)$ for filtering of groups, and 0 or q for each group, depending on their possibility of contribution. Demonstrably, the worst efficiency of the algorithm is realized when all of $\sim M^{3.528}$ contributing terms belong to different groups (The contributing terms of virial coefficients must be connected in the combination space, so this worst case is purely theoretical and is very unlikely to be realized). In this worst case, the algorithm needs

$$O(M^6/q) + O(M^{3.528}q). \quad (11)$$

The value of q can be adjusted to optimize the M dependence (mainly through adjusting N_c), and both terms have an equivalent dependency on M at $q=M^{1.236}$. The resultant $\sim O(M^{4.764})$ of the lower-bound computational complexity of our algorithm is far better than $\sim O(M^6)$. Of course, the efficiency of typical cases must be far better than this.

III. RESULT AND DISCUSSION

The algorithm of virial counting was implemented as a FORTRAN program in combination with the fast chain-generation algorithm. The program was executed on a clustered LINUX PC with each node having two 2.8 GHz Zeon processors and 2 Gbytes of memory (Bladecenter HS20, IBM Corp.) We set the value of N_c to 4 throughout the simulation because this setting was proven in a previous study to be good for extremely large chains. Roughly speaking, virial calculations of linear and simple comb polymers with up to 220–230 segments can be accomplished in a realistic time (2–4 days) in such a condition.

A special problem of calculation of the virial coefficients of a comb polymer is, as already reported,¹⁶ that the comb polymers are markedly aspherical. The A_2 of oblong objects is biased when their principal axis tends to be aligned. Similarly, an unnatural alignment of aspherical particles can engender an underestimation of A_3 .

Linear polymers also have asphericity. However, the effect of asphericity has been assumed to be negligible up to now. The principal axes of respective samples are not correlated. Therefore, the aspherical effect should disappear when it is averaged over many samples. This is particularly true for off-lattice methods. Moreover, this is especially true for long chains because the longer the chain is, the less memory of the starting point remains in the chain; a general alignment between samples becomes closer to randomness (the asphericity of individual samples might be stronger for longer chains). Apparently, the asphericity problem has, by far, greater importance in the case of the comb polymers; it is more aspherical and with shorter individual chains compared to the linear chains with the same number of segments.

A random swapping of axes is introduced to the program such that any samples subject to A_2 and A_3 calculations undergo one of the following three operations, randomly selected to cancel these effects out:

$$\begin{aligned} x \rightarrow y, \quad y \rightarrow z, \quad z \rightarrow x, \\ x \rightarrow z, \quad y \rightarrow x, \quad z \rightarrow y, \\ x \rightarrow x, \quad y \rightarrow y, \quad z \rightarrow z \text{ (identity transformation)}. \end{aligned} \quad (12)$$

The resultant two values of A_3 , with and without the operation, were compared to check the asphericity effect. The number of the segments was set to the largest size simulated for each topology. The A_3 of the HHH polymer turned out to be underestimated by the asphericity effect by 5%; it was the largest underestimation observed. Compared to 2.5% of underestimation observed for the H polymer, we can conclude that the larger the scale of the comb, the greater the effect of asphericity. On the other hand, the underestimation caused

by the asphericity of a linear polymer is only about 1%, which is our justification for not using direction randomization process in the previous papers. Because a marked asphericity effect is observed for combs, all values presented from this point on are those estimated using the randomization process.

The values obtained by full-scale simulations are shown in Table I for various configurations of polymers. All comb polymers and linear polymers longer than 85 are new reports. The values A_2M^2 and A_3M^3 are represented as “raw” data, which come directly from counting. The value $M=fl$ is the molecular weight (the number of segments in a polymer chain). The smallest number of the samples, 1800, was used for the HHH polymer, and 4000–15 000 is used for the other cases. The obtained values of A_2 and A_3 are plotted in a double-log manner in Figs. 2 and 3, respectively.

Actually, difficulties exist in finding literature related to the experimental estimation of the second and third virial coefficients. The only result we were able to find is related to the second virial coefficient of the H-shaped polymer¹⁹ in a review.¹ That study provides values of the penetration function of the H polymer

$$\Psi = \frac{A_2M^2}{4\pi^{3/2}N_A\langle r^2 \rangle_g^{3/2}} \quad (13)$$

in the range of 0.46–0.40. The ratio to the linear polymer

$$A_2(\text{H comb})/A_2(\text{linear}) \quad (14)$$

has value of 0.98–0.95 (the sample with the largest molecular weight showed 0.95).

On the other hand, our estimation of the penetration function ranges from 0.49 for $M=41$ to 0.43 for $M=221$. This result is consistent with the values obtained through experimentation. The ratio to the linear polymer turned out to be 0.91, a slightly smaller value than that obtained in the experiment. The review also introduced predictions based on the renormalization group.^{20,21} The predicted value of the penetration function was 0.429, a very good match to our result (including the value of 0.43 obtained for the longest chain). The predicted value of the ratio to the linear polymer was 0.949. Among the experimental values, this corresponds to the smallest and is closest to our result. In summary, our results on A_2 of the H-shaped polymer showed a very good match to the previous result. We were able to find no experimental results of A_3 for larger combs.

Using a plot similar to Fig. 3, Bruns tested the power-law behavior of A_3 of the linear polymer, $A_3 \propto M^{0.528}$, on various lattices, and concluded that the number of the segments in that simulation was insufficient for a good convergence. In the present study, we also simulated the linear polymer to increase the segment number to 225. It seems that the value of A_3 of the linear polymer converges to the expected power behavior. The plot for combs shows a good fit to the power behavior, and the slopes seem to converge at 0.528.

A convenient index of A_3 to discuss is the dimensionless factor g , which is defined using A_2 and A_3 as

TABLE I. Obtained second and third virial coefficients for linear polymers and comb polymers.

f^l ($f=1$)	$A_2 M^2$	A_2	$A_3 M^3$	A_3	g
9	28.2±0.4	0.35±0.005	349.4±6.3	0.48±0.009	0.439
17	81.9±1.3	0.28±0.004	2659.2±58.8	0.54±0.012	0.397
25	158.6±2.8	0.25±0.004	9581.5±275.9	0.61±0.018	0.381
33	255.3±4.5	0.23±0.004	24 612.1±654.4	0.68±0.018	0.378
41	369.3±6.8	0.22±0.004	50 447.9±1418.9	0.73±0.021	0.370
81	1181.7±32.9	0.18±0.005	501 759.7±20 793.8	0.94±0.039	0.359
121	2405.9±71.8	0.16±0.005	2 056 982.6±95 443.8	1.16±0.054	0.355
161	3874.7±88.1	0.15±0.003	5 343 115.5±190 117.8	1.28±0.046	0.356
201	5734.8±132.7	0.14±0.003	11 575 911.0±421 958.0	1.43±0.052	0.352
225	6988.1±160.5	0.14±0.003	17 098 094.0±582 833.7	1.50±0.051	0.350
H ($f=5$)					
41	334.6±2.7	0.20±0.002	49 348.0±671.1	0.72±0.010	0.441
61	658.5±6.0	0.18±0.002	187 315.1±2937.5	0.83±0.013	0.432
81	1076.2±10.3	0.16±0.002	494 416.5±8283.4	0.93±0.016	0.427
101	1569.0±15.2	0.15±0.001	1 045 062.8±18 130.1	1.01±0.018	0.425
121	2163.4±22.0	0.15±0.002	1 970 055.6±35 116.7	1.11±0.020	0.421
141	2807.8±28.6	0.14±0.001	3 318 853.0±60 982.4	1.18±0.022	0.421
161	3529.8±33.2	0.14±0.001	5 227 918.5±87 196.3	1.25±0.021	0.420
181	4317.8±80.5	0.13±0.002	7 775 423.0±257 921.3	1.31±0.043	0.417
201	5196.4±97.6	0.13±0.002	11 195 884.0±365 440.6	1.38±0.045	0.415
221	6112.2±122.1	0.13±0.003	15 485 433.0±562 173.4	1.43±0.052	0.415
HH ($f=8$)					
65	685.8±9.1	0.16±0.002	213 846.8±5003.4	0.78±0.018	0.455
97	1365.7±19.1	0.15±0.002	835 362.8±20 561.5	0.92±0.023	0.448
129	2220.8±32.7	0.13±0.002	2 187 875.2±57 018.8	1.02±0.027	0.444
161	3258.7±50.2	0.13±0.002	4 684 790.5±128 111.5	1.12±0.031	0.441
193	4486.1±67.3	0.12±0.002	8 873 674.0±239 625.6	1.23±0.033	0.441
225	5863.1±95.4	0.12±0.002	14 520 305.0±348 696.8	1.27±0.031	0.422
HHH ($f=11$)					
89	1102.1±19.7	0.14±0.002	560 344.5±17 427.7	0.79±0.025	0.461
133	2181.8±42.7	0.12±0.002	2 171 387.8±73 823.7	0.92±0.031	0.456
177	3582.4±70.5	0.11±0.002	5 893 973.5±203 275.4	1.06±0.037	0.459
221	5307.0±111.3	0.11±0.002	12 649 239.0±445 070.2	1.17±0.041	0.449

$$g = \frac{A_3}{MA_2^2}. \quad (15)$$

Thus far, numerous authors have investigated the value of g via both experimental and theoretical approaches. However, the previously reported values are scattered across a wide range, even in the simple case of the linear polymers in the good solvent limit. The value of g calculated from our data obtained for various comb polymers is shown in Fig. 4 along with experimental results already reported for linear polymers.^{22,23} Unfortunately, we were able to find no experimental data to compare with them. The excluded-volume-effect parameter z , defined as

$$z = (3/2\pi)^{3/2} (M)^{1/2} \beta, \quad (16)$$

is taken as the X axis because this is a convenient way to compare the simulation results with the experimental results. Here, the volume of each segment β was taken as 1. In our previous work, the limiting value for the linear polymer appeared to be near 0.30, which was consistent with experimental results. It is interesting that the values of the combs

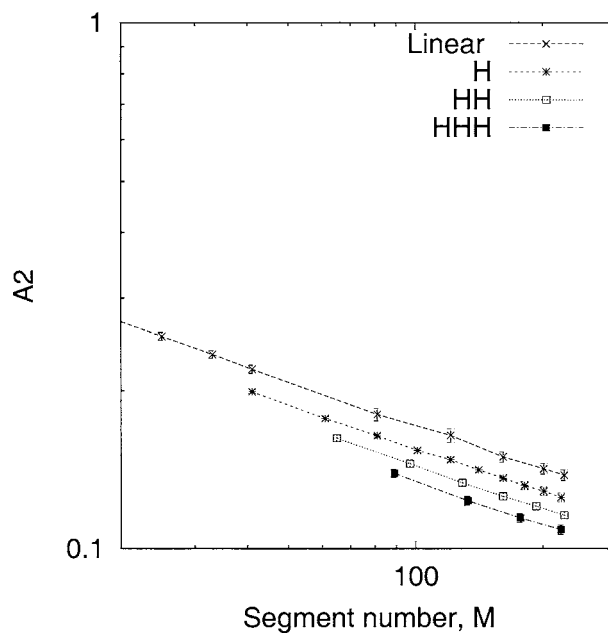


FIG. 2. Obtained second virial coefficients of various comb polymers plotted as functions of their number of segments.

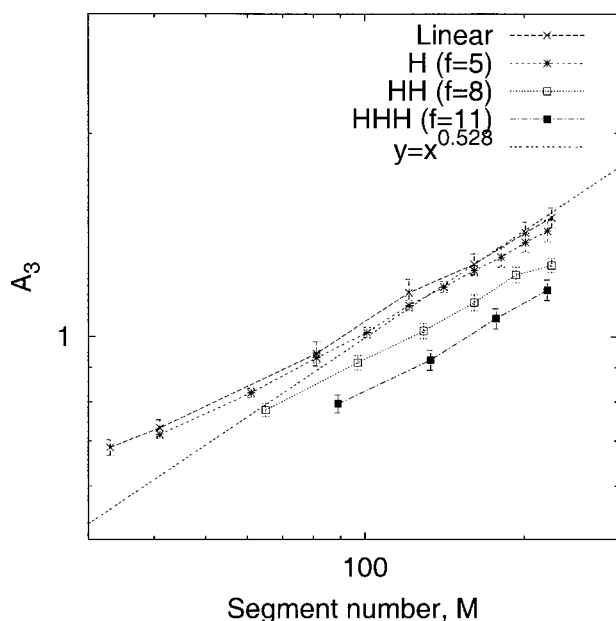


FIG. 3. Obtained third virial coefficients of various comb polymers plotted as functions of their number of segments. The power law of $A_3 \propto M^{0.528}$ is the one to which Bruns compared his result.

seem to converge to values that are larger than that of the linear polymer and which are dependent on their topology. Such a topological dependence has already been reported in experiments, but for star polymers.^{24,25}

Finally, we plot the comb polymers' gyration radii, A_2 and A_3 , as a function of comb length in Figs. 5–7. The comb length is the size of the “coarse-grained” comb, regarding each branch point and the arms directly emanating from it as a hypothetical repetitive unit. Therefore, the respective comb lengths of H, HH, and HHH polymers are 2, 3, and 4, and the size of each unit is represented by the length of a single arm, l . As clearly shown in these plots, these configurational and dimensional parameters of the comb polymers can be well characterized using the same power law of the linear polymer, as if the combs were a kind of short linear polymers comprising segments with a larger excluded volume.

Although experimental results of the gyration radius of the comb polymer have already been reported,²⁶ it is difficult

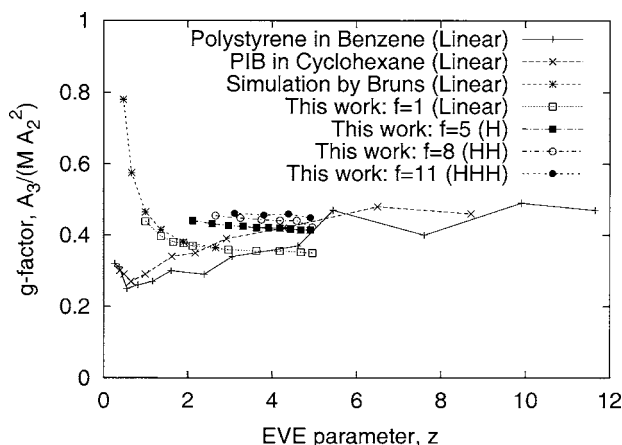


FIG. 4. The value of the g factor and its dependence on the excluded-volume-effect parameter $z = (3/2\pi)^{3/2}(M)^{1/2}\beta$.

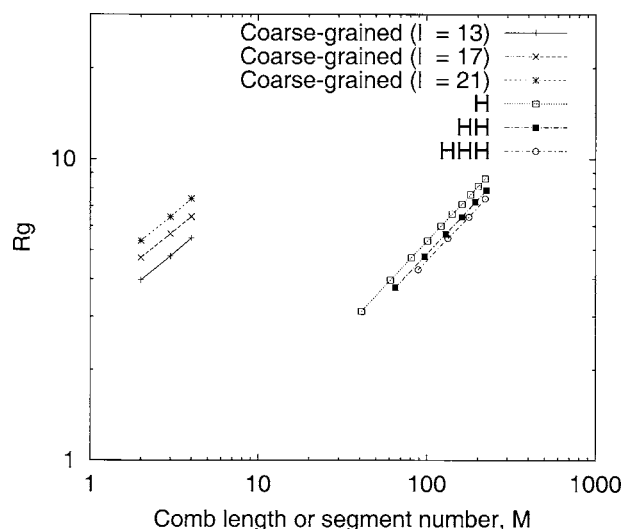


FIG. 5. In this figure, the gyration radii of the comb polymers are indicated as a function of their segment number and the “comb length,” which is the number of branch units.

to compare the result to our data because the comb length in our data is not sufficiently long to make the coarse-grained comb in its scaling region. A notable point that is shown clearly in the figures is that the power-law exponents of A_2 and A_3 of a coarse-grained chain seem to be exactly the same as those of the normal polymer, although the power-law exponent of the gyration radius of the coarse-grained polymer is smaller than that of the normal polymer. In Shiohara's report of computer simulations,⁴ the gyration radii of entire comb polymers as a function of “backbone length” (their backbone length is basically proportional to our comb length) converge to the power law similar to that of the linear polymer. However, in the same report, the comb polymers with long side chains required a longer backbone length for the convergence: short combs tend to have smaller values of exponents than the asymptotic value. This might partially explain the reduced value of the power-law exponent.

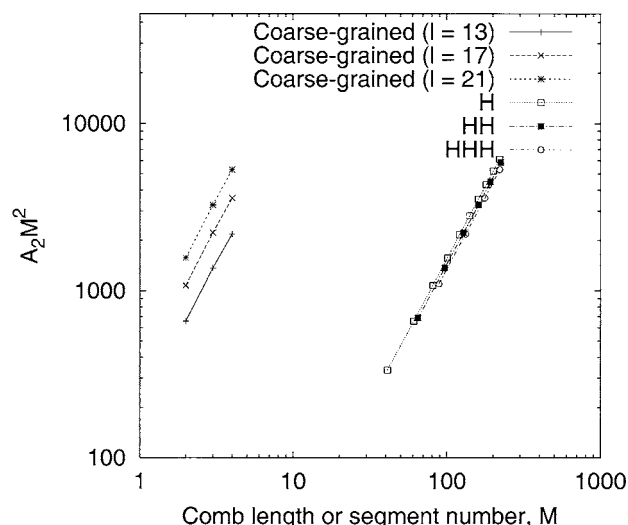


FIG. 6. In this figure, A_2 of the comb polymers are indicated as a function of their segment number and the comb-length, which is the number of branch units.

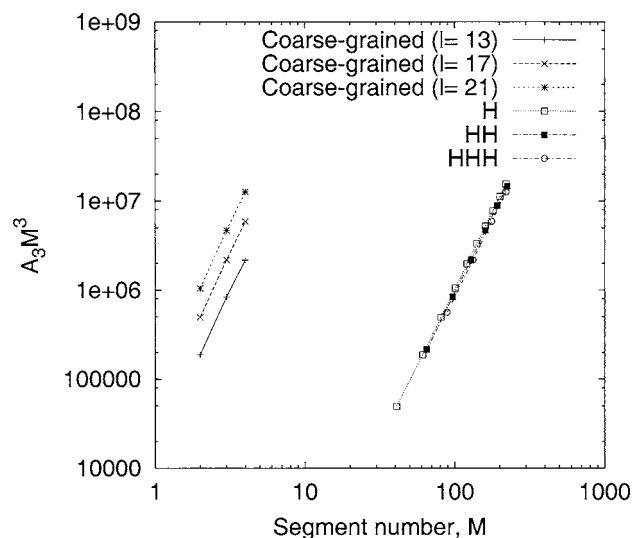


FIG. 7. In this figure, A_3 of the comb polymers are indicated as a function of their segment number and the comb length, which is the number of branch units.

IV. CONCLUDING REMARKS

Our previously proposed algorithm, which provides the A_3 estimation in a realistic time using counting contributing terms, was successfully applied to small combs. The result for the second virial coefficient of the H-shaped polymer is comparable to the experimental data reported before. The combs showed clear power-law behaviors with a great similarity to those of the linear polymer with a normal definition of segments when the branch units are regarded as segments.

ACKNOWLEDGMENTS

The authors are grateful to the staff and management of the Supercomputing Center at the IMR, Tohoku University for its support. This work was partially supported by “Spe-

cial Coordination Funds for Promoting Science and Technology” of the Japanese Ministry of Education, Culture, Sports, Science and Technology.

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