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Monte Carlo calculation of second and third virial coefficients of linear and star polymers on lattice

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An efficient algorithm for counting contributing terms in the calculation of second and third virial coefficients of the lattice polymer model was proposed. The algorithm was applied to linear and three-arm star polymers. The algorithm's efficiency was demonstrated, and the obtained results were compared to both experimental and computational results already reported. To the authors' best knowledge, the estimation of the third virial coefficient of the three-arm star polymer is the first reported. © 2002 American Institute of Physics. [DOI: 10.1063/1.1518688]

I. INTRODUCTION

The second and third virial coefficients of polymeric solutions have been of great interest in polymer physics. 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. Although the third virial coefficient has been evaluated experimentally for polymer systems, it is rarely dealt with by computer simulation. The main difficulty of virial coefficient calculations is the inevitable multidimensional integration which requires intensive computation. This tendency is even more apparent in the case of the higher-order virial coefficients.

One of the very few examples of such work is that of Bruns.¹ A straightforward method of calculation, assuming hard-core potential, was employed in his paper. However, this approach resulted in a severe limitation on the scale of the simulation. The only study that has paid close attention to the efficiency of such calculations was presented by Poland,² who utilized the symmetry of sample lattice chains in order to simplify the calculation. Poland has shown that such a calculation is effective for up to seven segments per chain. However, the improvement of efficiency enabled by Poland's simplification remains insufficient, if one wants to perform such a calculation on complicated polymer systems such as the star-shaped polymers.

In a noteworthy study by Vega *et al.*,³ the second, third, and fourth virial coefficients were calculated for the pearl-necklace model, which is an off-lattice model of contacting hard spheres. In the study, they utilized sampling of molecular shape and their relative positions, corresponding to the integral operations in the formulas of virial coefficients. Again, no effort was expended on the efficiency of the calculation, and they reported that they had to spend excessive time for their calculations.

There has been considerable work done on higher-order virial coefficients for nonpolymeric systems. One example considers the two-dimensional case of molecules with very simple shapes (hard convex bodies) compared to polymers.⁴ Apparently, the method used for such simple shapes is not applicable to our current purposes.

We were therefore motivated to develop an efficient algorithm for calculating virial coefficients of polymeric systems. In the present paper, a viable candidate algorithm is proposed and tested by applying it to linear- and three-arm star-polymers.

II. METHOD

Estimation formulas of virial coefficients, which take intermolecular potential as input, can be derived through the theory of cluster integral. 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 $\mathbf{r}_1, \mathbf{r}_2$,

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

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

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

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

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.

Since flexible polymer molecules do not have fixed shapes, 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.⁵ 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 also 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 overlapping each other. A sampled polymer molecule in the model is described as

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

where l is the number of the segments in each molecule, and i the index of the molecule in the system. Usually complete monodispersity is assumed, hence l 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:

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

A number of such polymer molecules or chains are generated according to pseudorandom numbers, and they form an ensemble of a system. The integrals already introduced in Eqs. (2) and (3) should be performed on large number of such sample chains, 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, denoted as chains 1, 2, and 3. The

integration/summation for A_2 is performed for each of three pairs of chain: 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) enables 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 is 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 $\sim O(l^2)$ of computational complexity.

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

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

Obviously, scanning all of these indices requires $\sim O(l^6)$ of computational complexity. At this point, the problem becomes very challenging in terms of computing. Regardless of the performance of the computer used for the simulation, $O(l^6)$ will soon become an intractable burden because the value of l must be sufficiently large in order to achieve reliable results in the scaling region. In addition, the sample number, N_{samp} , should be large enough for appropriate statistical convergence.

We arrived at a conclusion that a sophisticated algorithm needed to be developed before further study of this subject was pursued. Therefore, we tested several algorithms, including hash-searching and complicated clustering of the displacement vectors, and we discovered that the following algorithm was quite simple and effective.

The algorithm focuses on the more difficult of the problems, namely the A_3 counting. The $O(l^6)$ 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). Hence, when combinations are separated into groups of appropriate size, 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 combinations within the remaining groups are checked at the second stage. As 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 can be defined 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} , like $\mathbf{V} = \mathbf{R}(\mathbf{V}) + \mathbf{e}(\mathbf{V}) (|\mathbf{e}(\mathbf{V})| < d)$. Note that displacement vectors in a group are sharing the same \mathbf{R} hence 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 into Eq. (8) in place of the corresponding displacement vectors, to obtain an approximated value of the left-hand side (lhs) of Eq. (8). That is, the lhs of Eq. (8) turns out to be

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

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 cannot have a magnitude greater than d . This is a necessary condition, which 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 group of combination or not. Equation (10) can be used to screen out the unnecessary combination of indices effectively before Eq. (8) is applied.

Clearly, the result of the counting does not change from that of the original algorithm. An important point to discuss is how effectively the two-stage algorithm reduces the number of combinations. Since there is no information on the distribution of contributing terms in the combination space, the point would be very difficult to discuss. We leave the resolution of this point to future study, and confine ourselves here to the task of optimization of the adjustable parameter of the algorithm, N_c . Considering how the algorithm functions, it is believed that the value of N_c greatly influences efficiency.

III. RESULT AND DISCUSSION

The algorithm was implemented as a FORTRAN program, in combination with a fast chain-generation algorithm.⁶ The program was executed on a Compaq ES40 workstation with a 700 MHz CPU and 2 Gbytes of memory.

Although we had strong confidence in the equivalence between the two algorithms, a test was of course necessary. Therefore, the old algorithm was also implemented in the program such that the results were automatically cross-checked for each sample chain configuration. The program was configured to report any disagreement between the algorithms, and executed for about a million of $f=1$ and $f=3$ sample chains. The disagreement between the results of the two algorithms was never detected. This fact proved that our

TABLE I. Performance of the developed algorithm measured in terms of the elapsed time (in seconds).

Simulated system	Conventional algorithm	$N_c=2$	$N_c=3$	$N_c=4$	$N_c=5$
$l=25, N_{\text{samp}}=5000$	1118	261	314	440	622
$l=49, N_{\text{samp}}=500$	2719	471	401	607	610
$l=73, N_{\text{samp}}=100$	4266	557	351	527	873

new algorithm is not an approximation: its result is always the same as the original. With this confirmation, we proceeded to the next phase.

First, we performed a series of small-scale simulation runs in order to check the improvement in efficiency. By means of these simulations, the optimum N_c and its dependency on the value of l could be investigated. The value of A_2 and A_3 of a linear chain was calculated for various combinations of l and N_c . The number of the samples, N_{samp} , was adjusted such that this preliminary simulation was completed within an appropriate time. The configuration of the program was slightly changed and either of the two algorithms was actually executed in a run to measure the performance separately. The time elapsed for the entire simulation, including the time required for chain generation, is shown in Table I. The “conventional” algorithm given in Table I is an exhaustive counting of displacement vectors as a control case. In the case of $l=25$, the improved algorithm was clearly advantageous, and the best setting of N_c was as low as 2. An even better performance was observed when the length of the chain was increased to 49 at $N_c=3$. In the case of $l=73$, the improved algorithm demonstrated about 12-fold acceleration, and the best value of N_c was still 3. This result implies that the optimum value of N_c is an increasing function of l as expected, although the increase of N_c is very slow. We set the value of N_c to 4 throughout the full-scale simulations, expecting that the optimum would be close to 4 in the case of simulating longer chains.

The values obtained by full-scale simulations are shown in Table II in the case of linear and three-arm star polymers. The values A_2M^2 and A_3M^3 are represented as “raw” data, which come directly from the counting. The value $M=fl$ is the molecular weight, defined as the number of segments in a polymer chain. The number of the samples was always 16 666, which indicates that the number of chains generated as samples was $\sim 50\,000$.

Roughly speaking, these values were in accord with our previous results.^{5,7,8} The only data we have previously obtained on A_3 were the result of an indirect measurement⁸ (not based on counting but on estimation of the osmotic pressure). This difference might have led to the discrepancy. In addition, the A_3 data reported by Bruns¹ should also be compared to our data. The plot of A_3 versus the segment number is shown in Fig. 1 in a double-log manner. Bruns drew the same plot for a linear chain on various lattices in his paper to check the putative power-law behavior of $A_3: A_3 \propto l^{0.528}$. His plot revealed power-law behavior but with an exponent of a far smaller value than 0.528. Bruns attributed this discrepancy to the small number of segments he employed (the

TABLE II. Obtained second and third virial coefficients for linear- and star-shaped polymers.

fl	$A_2 M^2$	A_2	$A_3 M^3$	A_3	g factor
$(f=1)$					
25	146.3 ± 0.6	0.23 ± 0.001	8981.8 ± 54	0.57 ± 0.003	0.42 ± 0.06
37	287.7 ± 1.1	0.21 ± 0.001	33672.8 ± 232	0.66 ± 0.005	0.41 ± 0.07
49	468.5 ± 2.7	0.20 ± 0.001	87394.3 ± 507	0.74 ± 0.004	0.40 ± 0.17
61	685.6 ± 3.5	0.18 ± 0.001	184611 ± 1271	0.81 ± 0.006	0.39 ± 0.15
73	935.2 ± 6.1	0.18 ± 0.001	341035 ± 3741	0.88 ± 0.010	0.39 ± 0.15
85	1217.1 ± 9.4	0.17 ± 0.001	573677 ± 4436	0.93 ± 0.007	0.39 ± 0.25
$(f=3)$					
34	271.8 ± 1.0	0.22 ± 0.001	32679.6 ± 234	0.76 ± 0.006	0.44 ± 0.06
46	441.5 ± 1.9	0.20 ± 0.001	84689.4 ± 489	0.82 ± 0.005	0.43 ± 0.08
58	645.2 ± 3.8	0.19 ± 0.001	178744 ± 1426	0.87 ± 0.007	0.43 ± 0.11
70	880.9 ± 4.0	0.17 ± 0.001	330239 ± 2531	0.92 ± 0.007	0.43 ± 0.09
82	1147.3 ± 9.3	0.17 ± 0.001	556624 ± 5569	0.97 ± 0.010	0.42 ± 0.22

conjecture on the power-law behavior was based on a scaling theory).

However, in the present study, we extended the segment number to 85, and the plot shown in Fig. 1 remains at distinctive power-law behavior with an exponent far from 0.528. This discrepancy cannot be explained by the estimation error given in Fig. 1. It is possible that Bruns's simulation was actually close to the asymptote, and that the true power-law behavior actually has the exponent lower than 0.528. Even if this was not the case, it should be noted that the convergence of the value of A_3 was extraordinarily slow, and that reaching the true scaling regime would in any case be very difficult. The same plot for a three-arm star polymer revealed an even slower convergence (or an even lower exponent). Probably, the number of the segments should be increased greatly to make each of three arms long enough for a good convergence. It seems the only way to realize such simulations and obtain the reliable exponent of the star polymers is with the use of our algorithm.

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

$$g = \frac{A_3}{MA_2^2}. \quad (11)$$

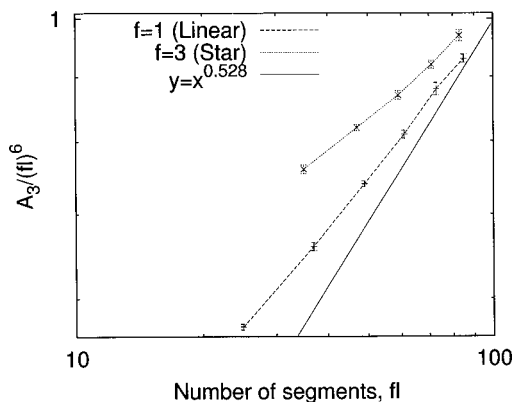


FIG. 1. The third virial coefficient plotted against the reciprocal of the segment number. The power law of $y \propto x^{0.528}$ is the one Bruns was comparing his result with.

Thus far, many 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 l for linear- and three-arm star polymers is plotted in Fig. 2, along with the data from previous studies, including experimental data. The excluded-volume-effect parameter z , defined as

$$z = (3/2\pi)^{3/2} (fl)^{1/2} \beta, \quad (12)$$

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 to be 1. The limiting value for the linear polymer appears to be near 0.30. This value is close to that obtained via a renormalization group method by des Cloizeaux.⁹ The experimental results for linear polymers are available for polystyrene in benzene¹⁰ and polyisobutylene in cyclohexane.¹¹ Again, our data are in good agreement with these data in the case of linear polymers.

One very interesting aspect of this study was that the plot for three-arm star polymer did not really appear to converge at the same point as the linear polymer. Such an effect

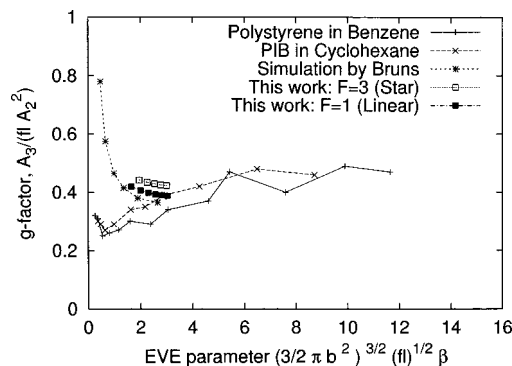


FIG. 2. The value of the g factor, and its dependence on the excluded-volume-effect parameter $z = (3/2\pi)^{3/2} (fl)^{1/2} \beta$.

has already been observed in an experiment of star-shaped polystyrene in benzene^{12,13} and the increased segment density around the central part of the star polymers is believed to be relevant to the effect. Dependence of the chain connecting pattern or the topology of polymer chains on their A_2 and A_3 behavior continues to be of great interest.

IV. CONCLUDING REMARK

Our proposed algorithm provides the A_3 estimation by means of counting contributing terms in a realistic time. The result is comparable to the experimental data reported before. We are considering several future possible alterations of the algorithm. An extension for cluster-integral of higher order, that is A_4 , A_5 , ..., is under consideration. To realize these studies, the algorithm should undergo further sophistication by vector/parallelization, hierarchical grouping, and probably by a sampling of segment-segment vector.

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