

Interactions between ring polymers in dilute solution studied by Monte Carlo simulation

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The second virial coefficient, A_2 , for trivial-ring polymers in dilute condition was estimated from a Metropolis Monte Carlo (MC) simulation, and the temperature dependence of A_2 has been discussed with their Flory's scaling exponent, ν , in $R_g \propto N^\nu$, where R_g is radius of gyration of a polymer molecule. A limited but not too small number of polymer molecules were employed in the simulation, and the A_2 values at various temperatures were calculated from the molecular density fluctuation in the solution. In the simulation, the topology of ring polymers was kept, since chain crossing was prohibited. The excluded volume effects can be screened by the attractive force between segments, which depends on the temperature, T_α , defined in the Metropolis MC method. Linear and trivial-ring polymers have the ν value of $1/2$ at $T_\alpha = 10.605$ and 10.504 . At $T_\alpha = 10.504$, the excluded volume effects are screened by the attractive force generated between segments in a ring polymer, but the A_2 value for ring polymers is positive. Thus, the temperature at $A_2 = 0$ for a ring polymer is lower than that at $\nu = 1/2$, and this fact can be explained with the following two reasons. (a) R_g value for a ring polymer is much smaller than that for a linear polymer at the same temperature and molecular weight, where interpenetration of a ring polymer chain into neighboring chains is apparently less than a linear chain. (b) The conformation of trivial rings can be statistically described as a closed random walk at $\nu = 1/2$, but their topologies are kept, being produced topological constraints, which strongly relate not only to the long-distance interaction between segments in a molecule but also the inter-molecular interaction. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4906556>]

I. INTRODUCTION

Many studies have been accumulated on the chain conformations of ring molecules by experiments, simulations, and theories in contrast to those of linear molecules, and it is well established that a ring chain adopts a compact conformation than a linear chain with the same molecular weight in solutions or in bulk due to its topological constraint.

The radius of gyration of a polymer molecule, R_g , can be scaled with the number of segments in a polymer molecule, N , as

$$R_g \propto N^\nu, \quad (1)$$

where ν is the Flory's scaling exponent.^{1,2} The scaling behavior of polymer chains is classified with the ν values, and the temperature at $\nu = 1/2$ is defined as θ -temperature. At $\nu = 1/2$, the trajectories of a linear polymer can be described as a random walk. The behavior of the polymer molecule can be explained with the phantom chain model (PCM) at the θ -condition, where the polymer chains are allowed to cross each other, and the magnitude of chain conformation entropy is maximum. If the trajectories of a linear polymer in a dilute

solution at the θ -condition can be described as the PCM, its excluded volume is screened completely. The trajectories and location of a polymer molecule in the solution are not influenced by the other molecules, where the chain trajectory can be described as a random walk and the second virial coefficient, A_2 , is zero.

The number of topologies of ring polymers is infinite, and the dimension is influenced by their topologies. Grosberg³ discussed the ν value for zero-thickness but non-phantom ring polymers, and concluded that the ν value is the same as that for self-avoiding linear polymers, i.e., $\nu = 0.588$. Dobay *et al.*⁴ generated many closed non-self-avoiding random trajectories, where they were divided into several groups depending on knot types. Each group with different topology has ν value of 0.588 . Matsuda *et al.*⁵ and Moore *et al.*⁶ generated many conformations of ring polymers with zero-thickness but non-phantom chains. Thus, because of the topological swelling, ring polymers with fixed topology have the ν value of 0.588 .

The difference of A_2 values between linear and ring polymer solution has been discussed for a long time. Kamenetskii *et al.*⁷ generated many closed self-avoiding walks, and reported the probability of knot formation by the Alexander polynomials,⁸ where the dependence of a free energy, the potential energy between two chains, on the

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inter-chain distance was evaluated. Iwata *et al.*^{9–11} discussed topological effects in ring polymers and estimated the A_2 values with the evaluation of Gauss linking coefficient. As the theoretical studies, des Cloizeaux¹² and Tanaka¹³ argued topological effects in solution, while Deguchi *et al.*¹⁴ reported statistics of random knots and links with a Monte-Carlo (MC) simulation. Recently, Ida *et al.*^{15,16} evaluated A_2 values between semi-flexible ring polymers with a MC simulation, where the A_2 values were calculated from the potential energy and the interpenetration function between two rings, and the results were applied to those for ring polystyrene in the range of $M_n \leq 10^5$. A large number of conformations were generated in their studies^{9–11,14–16} and were classified by their topologies using the Gauss linking coefficient.¹⁷

Suzuki *et al.*^{18,19} reported that the topological constraint in trivial, 3_1 -, and 5_1 -knot ring polymers in the limited but fairly large N region, $N \leq 2048$, where the ring polymers were isolated in the three dimensional lattice. The topology of ring polymers was kept in the studies, since polymer chains have the excluded volumes and chain crossing was prohibited in the simulation. The temperatures T at $\nu = 1/2$ for linear and three ring polymers with different topologies show the following relative relationship:

$$T_{\text{linear}} > T_{\text{trivial}} > T_{3_1} \geq T_{5_1}. \quad (2)$$

The segmental distribution functions for trivial-, 3_1 , and 5_1 ring polymers under the conditions of $\nu = 1/2$ were compared in the finite N region in the successive study,²⁰ where the topologies were fixed. The distribution function for a trivial ring polymer at $\nu = 1/2$ can be described as a Gaussian function, with a closed random walk.

The θ -temperatures of ring polymers were observed with scattering methods by several groups,^{21–23} and they concluded that the A_2 values of ring polymers at the θ -temperature of a linear polymer, $T_\theta(L)$, are positive. This means that the excluded volume of ring polymer molecules cannot be screened completely by the attractive force between molecules at $T_\theta(L)$; the intermolecular interaction is repulsive force and the density fluctuation of molecules remains.

Thus, at $T_\theta(L)$, the ν value for a isolated trivial-ring polymer is larger than $1/2$. At $\nu = 1/2$ for a trivial-ring polymer, its conformations can be described as a closed-random walk. In this study, the A_2 value dependence of trivial-ring polymers on the temperature has been evaluated from a MC simulation, which was calculated from the conformations of polymer molecules and the density fluctuation of molecules in dilute solutions. It should be noted that polymer chains employed in this study keep their own topology, because each polymer segment bears the excluded volume. Thus, neither the topology of ring polymers can be changed by themselves nor two or more rings can create links, therefore, the A_2 value can be evaluated merely concerning with the topological constraints.

The lattice size is 256 with the three-dimensional periodic boundary conditions, and the number of molecules on the lattice is M . The results in this study were obtained under a limited condition; N is fixed to 1024 and M varies from 4 to 16. The chain length of $N = 1024$ in this study approximately corresponds to $M_n = 3.5 \times 10^5$ of polystyrene. Though the molecular weight does not reach the asymptotic region,²⁰ this

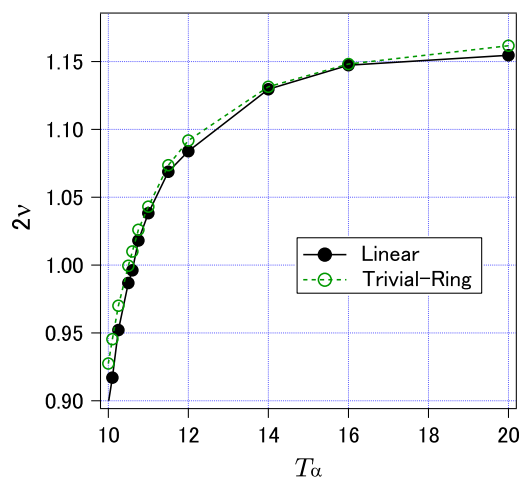


FIG. 1. The temperature dependence of 2ν values for linear and trivial-ring polymers. The 2ν values for linear and trivial-ring polymers become unity at $T_\alpha = 10.605$ and 10.504 , respectively.

must be the limit molecular weight range where well-defined ring molecules can be obtained by experiments.

II. SIMULATION

A. Simulation Method

An efficient simulation algorithm is required, because we try to obtain the A_2 values from scattering functions for linear and trivial-ring polymers at various temperatures and large N . The general idea of the simulation algorithm used in this study was introduced in the previous papers,^{18–20} where polymer segments bearing their excluded volumes were placed on lattice points of a face-centered-cubic (FCC) lattice. The segments are connected with bond and its length is $\sqrt{2}$ which is the distance between the nearest neighboring lattice points. Chain crossing is prohibited only with this rule, because FCC lattice is a close packed structure.

We employ the Metropolis MC method, and the procedure of the algorithm was explained in detail in the previous papers.^{18–20} Polymer beads can move not only with the local

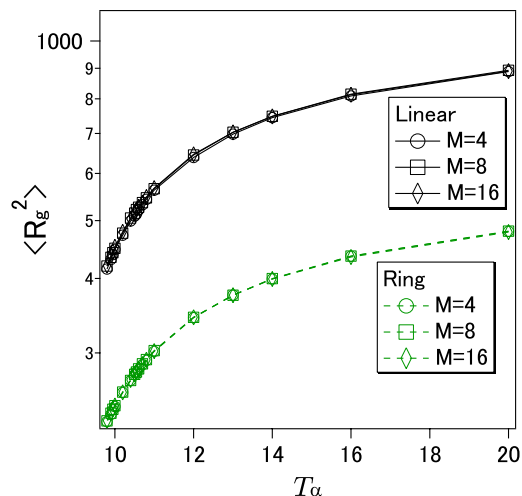


FIG. 2. Variation in $\langle R_g^2 \rangle$ against T_α for linear and ring polymers at $M = 4$, 8, and 16, where M is the number of polymer molecules on the lattice.

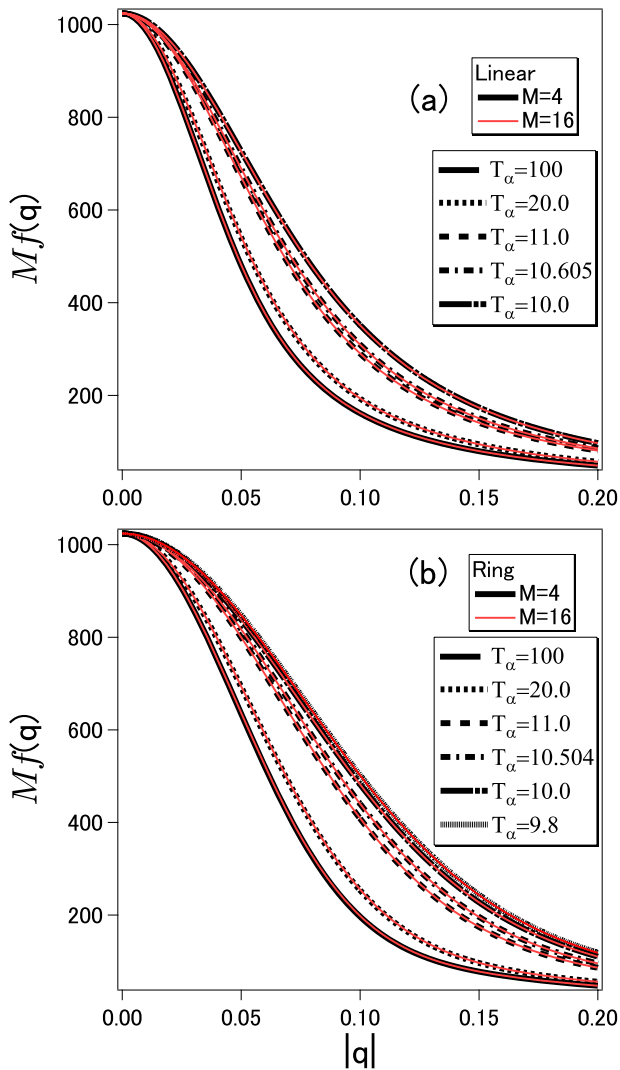


FIG. 3. Scattering intensity curves, $Mf(\mathbf{q})$ vs $|\mathbf{q}|$ in Eq. (A7), for (a) linear and (b) ring polymers at various temperature for $M = 4$ and 16.

motions but also with the trans-locations in the algorithm. A polymer beads is selected randomly for the transition from initial to trial positions in one MC step. If the trial position is occupied by the other beads, the trial is rejected. Probability p of the transition is defined as

$$p = \begin{cases} 1 & \text{if } \Delta E < 0, \\ \exp[-\Delta E/(k_b T)] & \text{otherwise,} \end{cases} \quad (3)$$

where ΔE is the energy change between initial and trial conformations, i.e., $\Delta E = -(E_{\text{trial}} - E_{\text{initial}})$, and k_b and T are the Boltzmann constant and absolute temperature, respectively. T_α is the reduced temperature, $T_\alpha = k_b T$. The number of segments at the first and the second nearest lattice points of the selected segment are $n_{1\text{st}}$ and $n_{2\text{nd}}$, respectively. E_{initial} and E_{trial} are enthalpic energy of the segment at initial and trial positions. The energy is defined as $n_{1\text{st}} + n_{2\text{nd}}/2$, where they are inversely proportional to the square of the distance between segments. In the previous papers, the enthalpic energy was concerned with the beads contact only, that is, $n_{2\text{nd}} = 0$. In this paper, $n_{2\text{nd}}$ is counted, because we perform simulations with many polymer molecules in the system.

The lattice size is 256 with the three-dimensional periodic boundary conditions. A limited but not too small number of polymer molecules are employed in the simulation: $4 \leq M \leq 16$, where the segment density, C_m , is in the range of $4.88 \times 10^{-4} \leq C_m \leq 1.95 \times 10^{-3}$ [segments/lattice point] at $N = 1024$.

Many snapshots were obtained at each interval, 2.7×10^3 [MC steps/segment]. The ensemble average of the square of the radius of gyration of a polymer molecule, $\langle R_g^2 \rangle$, is defined as

$$\langle R_g^2 \rangle = \left\langle \frac{1}{N} \sum_{i=1}^N |\mathbf{r}_{cm} - \mathbf{r}_i|^2 \right\rangle, \quad (4)$$

$$\mathbf{r}_{cm} = \frac{1}{N} \sum_{i=1}^N \mathbf{r}_i,$$

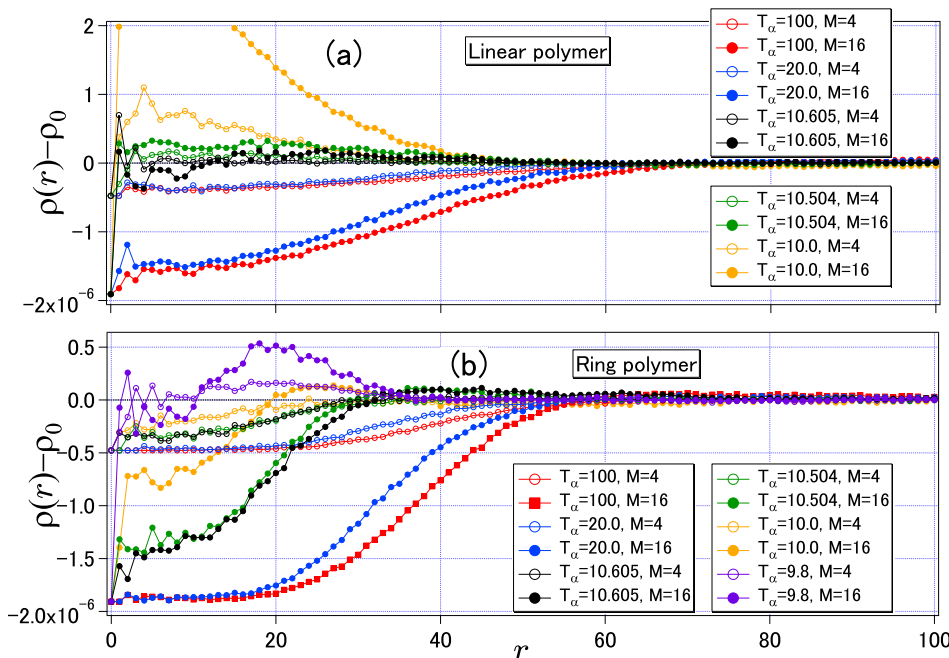
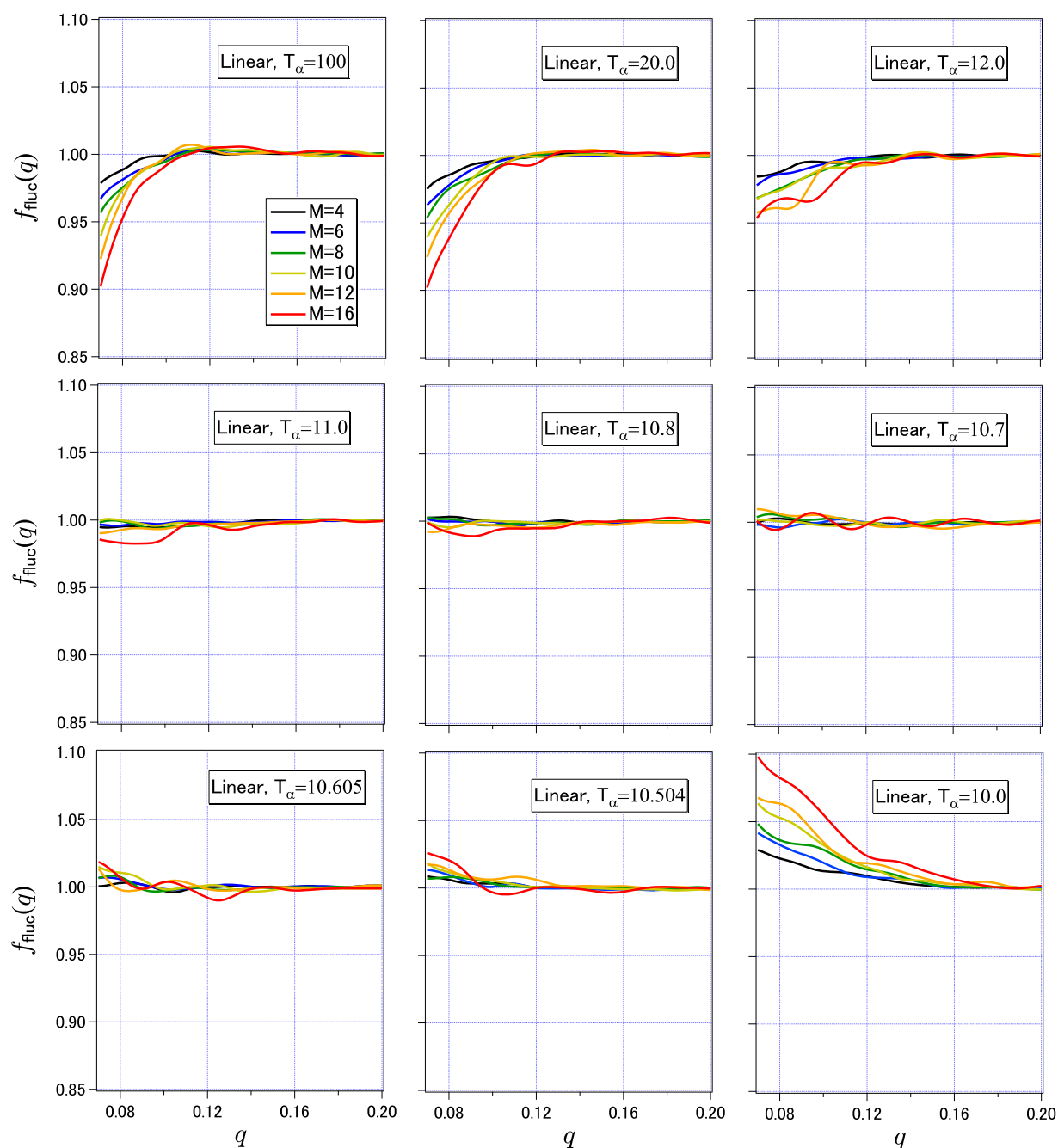


FIG. 4. Distribution function $P(r) = (\rho(r) - \rho_0)$ vs. r for (a) linear and (b) ring polymers.

FIG. 5. Scattering intensities, $f_{\text{fluc}}(q)$, vs. q at various temperatures and M .

where \mathbf{r}_i and \mathbf{r}_{cm} are the position vectors of the i th bead in a chain and that of the center of mass of the chain, respectively. Radial distribution functions of the polymer molecules were obtained from the snapshots with the three-dimensional periodic boundary condition and their ensemble averages were calculated.

The values obtained are the ensemble averages of the 128 simulation jobs for each condition, which were confirmed to be essentially the same as those of the 64 jobs. Each simulation job was for 24 h with an Intel Xeon processor. The computations were performed on the Central Computing system hosted by the Computing Research Center of the High Energy Accelerator Research Organization (KEK).

B. θ -temperature of isolated linear polymers

The 2ν values were obtained from the slopes of the double-logarithmic plots of $\langle R_g^2 \rangle$ and N . Fig. 1 shows the temperature dependence of 2ν values for isolated linear and trivial-ring polymers, which were obtained in the range of $512 \leq N \leq 2048$. Linear and trivial-ring polymers have the ν value of $1/2$ at $T_\alpha = 10.605$ and 10.504 , respectively. It is noted that these values were obtained from an isolated polymer molecule; interaction among segments in a molecule is only concerned and intermolecular interaction cannot be defined. In this study, θ -temperature is defined as $T_\alpha = T_\theta(L) = 10.605$, where the ν value for linear polymers is $1/2$.

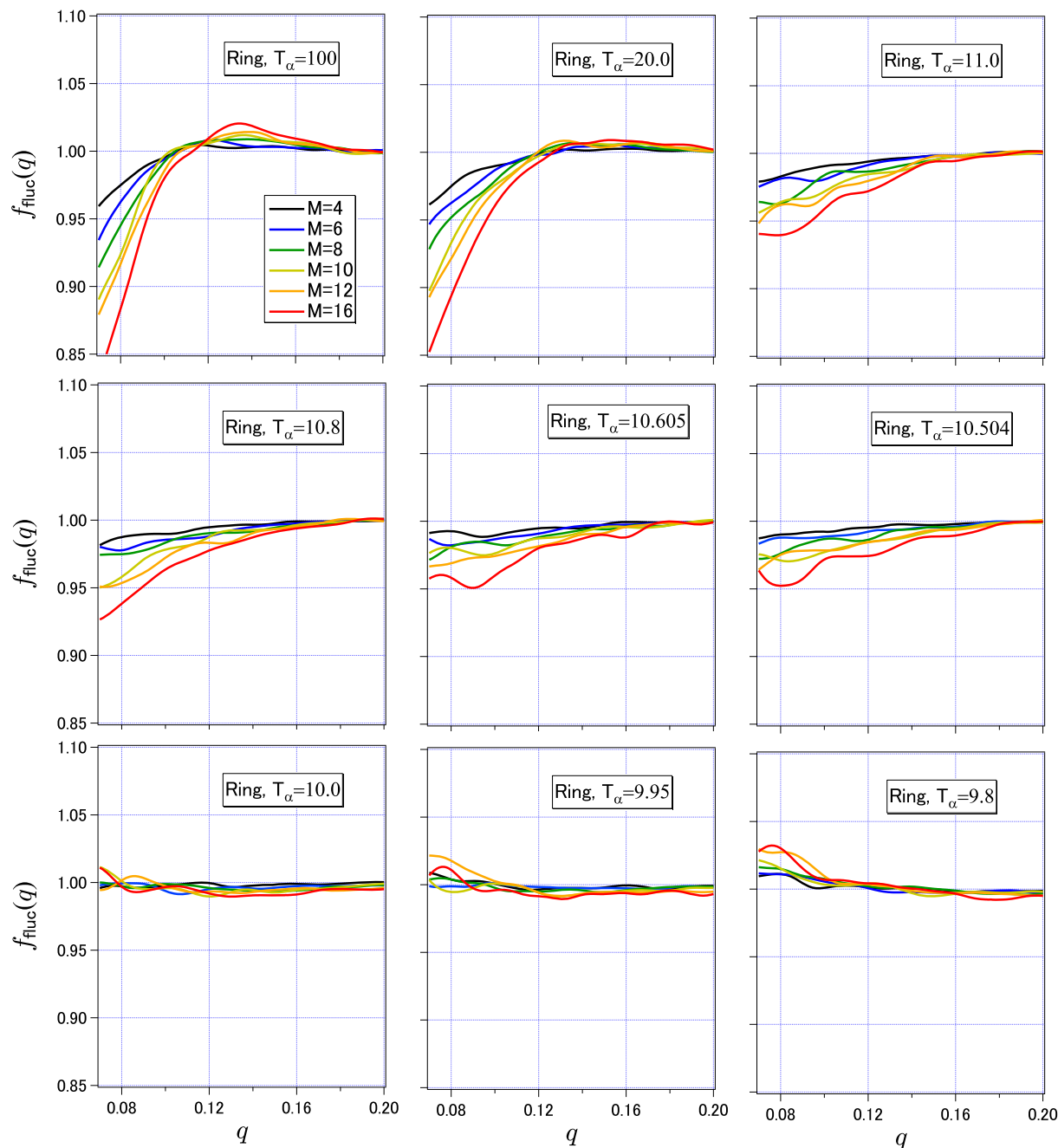


FIG. 5. (Continued.)

III. RESULTS AND DISCUSSION

A. Relationship between scattering intensity from polymers in dilute solution and second virial coefficient

The A_2 values obtained in this paper are at $N = 1024$. Inverse scattering intensity, $I^{-1}(q)$, for dilute polymer solution in small q region is given^{1,24} as

$$I^{-1}(q) = \frac{1}{N} \left(1 + \frac{R_g^2}{3} q^2 + \cdots \right) (1 + 2NA_2C_m + \cdots). \quad (5)$$

The principal parts of the first parenthesis in Eq. (5), $1 + R_g^2 q^2/3$, depend on the averaged conformation of chains,

and can be ruled by the $\langle R_g^2 \rangle$ values, while those of the second parenthesis in Eq. (5), $1 + 2NA_2C_m$, reveal the intermolecular interactions, and include the second virial coefficient, A_2 . Since we treat dilute polymer solutions in this study, the third and higher virial coefficients are ignored.

If the higher order terms with respect to q in the first parenthesis are ignored and the derivative of $I^{-1}(q)$ with respect to C_m is executed, we have Eq. (6),

$$\frac{d[I^{-1}(q)]}{dC_m} = \frac{1}{N} \left(1 + \frac{R_g^2}{3} q^2 \right) 2NA_2. \quad (6)$$

If polymer solutions can be treated under dilute condition, R_g at each temperature does not depend on C_m , and hence, Eq. (6)

reveals that $d[I^{-1}(q)]/dC_m$ is simply proportional to A_2 . The relationship in Eq. (6) is used for data analysis in this study.

B. Inverse scattering intensities for polymers in dilute solutions estimated by the simulation

Scattering functions for polymer aggregates in dilute solutions estimated by simulation will be explained in detail in the Appendix, where the value of $f(\mathbf{q})^2$ and $f_{\text{fluc}}(q)$ in Eq. (A7) express the scattering intensities from a polymer molecule isolated in a dilute solution and the magnitude of density fluctuation of polymer molecules, respectively.

The inverse scattering intensity, $I_{\text{sim}}^{-1}(q)$, can be obtained from Eq. (A7) as

$$\begin{aligned} I_{\text{sim}}^{-1}(q) &= \left(M f(\mathbf{q})^2 \left[1 + \int_0^R 4\pi r^2 (\rho(r) - \rho_0) \frac{\sin qr}{qr} dr \right] \right)^{-1} \\ &= [M f(\mathbf{q})^2]^{-1} f_{\text{fluc}}^{-1}(q). \end{aligned} \quad (7)$$

Since the $[M f(\mathbf{q})^2]^{-1}$ value at each temperature does not depend on C_m under dilute condition, and the derivative of $I_{\text{sim}}^{-1}(q)$ with respect to C_m is executed, and we have Eq. (8),

$$\frac{d[I_{\text{sim}}^{-1}(q)]}{dC_m} = [M f(\mathbf{q})^2]^{-1} \frac{d[f_{\text{fluc}}^{-1}(q)]}{dC_m}. \quad (8)$$

From Eqs. (6)–(8), the slope of $I_{\text{sim}}^{-1}(q \rightarrow 0)$ gives $2NA_2$.

If attractive force between polymer molecules is dominated, that is, it exceeds the excluded volume effects, polymer molecules are attracted to each other. Under this condition, the value of $f_{\text{fluc}}^{-1}(q)$ is smaller than unity and A_2 is negative; the polymers are in a poor solvent. Alternatively, if repulsive force between polymers works, $f_{\text{fluc}}^{-1}(q)$ is larger than unity and A_2 is positive; they are in a good solvent. At the particular point of $A_2 = 0$, the repulsive force is screened completely by the attractive force between polymer molecules; $d[f_{\text{fluc}}^{-1}(q)]/dC_m$ in Eq. (8) is zero.

C. Density fluctuation of polymer molecules in dilute solution

The $\langle R_g^2 \rangle$ values for linear and ring polymer at various T_α and M were estimated from the conformations of chains, and they are shown in Fig. 2. It is apparent that the $\langle R_g^2 \rangle$ values for ring polymers are much smaller than those for linear polymers at the same T_α , and they show definite temperature dependence, while they do not show M dependence, indicating that polymer molecules are in dilute solutions. Therefore, it is reasonable that the $\langle R_g^2 \rangle$ values are the ones at infinite dilution; $M \rightarrow 1$.

Fig. 3 compares $Mf(\mathbf{q})$ in Eq. (A7) against $|\mathbf{q}|$ at $M = 4$ and 16. It is evident that $Mf(\mathbf{q})$ for $M = 4$ is well superimposed on those for $M = 16$. This result implies that statistically averaged conformations of polymer molecules are not influenced by the C_m values in the range of $4 \leq M \leq 16$.

Fig. 4 shows the distribution function, $P(r) = (\rho(r) - \rho_0)$, vs. r for (a) linear and (b) ring polymers for various M and T_α . According to the definition in Eq. (A4), the polymer molecule located at $r = 0$ is not counted in the function, and we reach $P(r) \rightarrow 0$ in the large r region. At the θ -

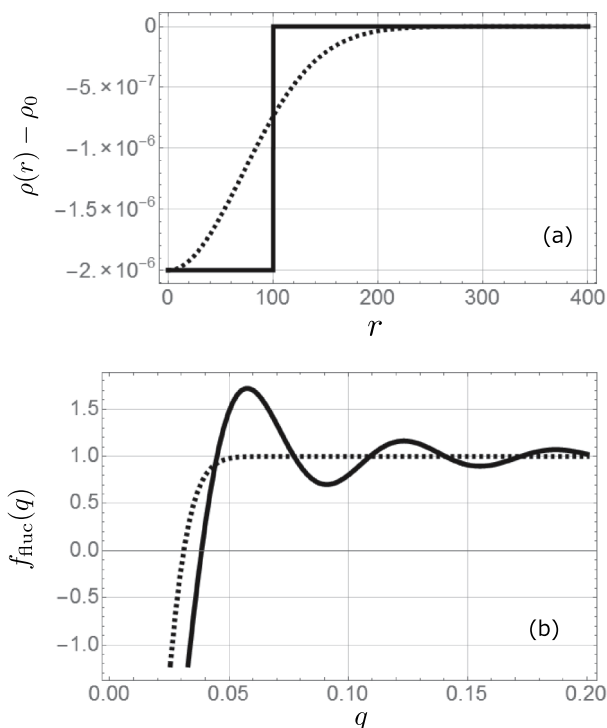


FIG. 6. (a) Two ideal examples of density distribution functions of molecules, red: a rectangle in the range of $0 \leq r \leq 100$, blue: a gauss function, $-2 \times 10^{-6} \exp[-(r/100)^2]$, and (b) their scattering functions.

condition for linear polymers, $T_\alpha = T_\theta(L) = 10.605$, $P(r) \sim 0$ for linear polymers is attained except near $r = 0$. The functions, $P(r)$, for linear polymers in the range of $T_\alpha > T_\theta(L)$ are monotonically increased from negative to zero with increasing r , implying that repulsive force between polymer molecules is working. Alternatively, the distribution functions at $T_\theta = 10.0$ are monotonically decreased with r , because attractive force between polymer molecules is effective. These results for linear polymers are quite reasonable, and random coils of linear polymers can be overlapped easily. At $T_\theta(L)$, $P(r)$ for ring polymers are evidently negative in the range of $r \leq 30$. At $T_\theta(L)$, ring polymer molecules are dominated by the repulsive force between molecules in a short distance much shorter than $\langle R_g^2 \rangle^{1/2}$, while $P(r)$ for ring polymers are approximately the same as those for linear polymers at the outside of the repulsive force region. At T_α is 10.0 or 9.8, $P(r)$ for ring polymers have negative values in the very small r region, where attractive force is working up to at around $r = 20$.

Fig. 5 shows the $f_{\text{fluc}}(q)$ defined in Eq. (A7) vs. q for linear and ring polymers at various temperatures, where $f_{\text{fluc}}(q)$ are obtained from the $P(r)$ values in Fig. 4. It is noted that $f_{\text{fluc}}(q)$ reflects only the magnitude of the density fluctuations of molecules, that is, the A_2 values obtained from $f_{\text{fluc}}(q)$ can be the measure of the intermolecular interactions. Since the scattering intensities for linear polymers in the small q region at high temperature region are decreased with increasing M values, A_2 should be positive. On the other hand, those at low temperature region are increased with increasing M , where A_2 is negative.

Scattering functions shown in Fig. 5 are more or less oscillated. Fig. 6(a) compares two ideal examples of density

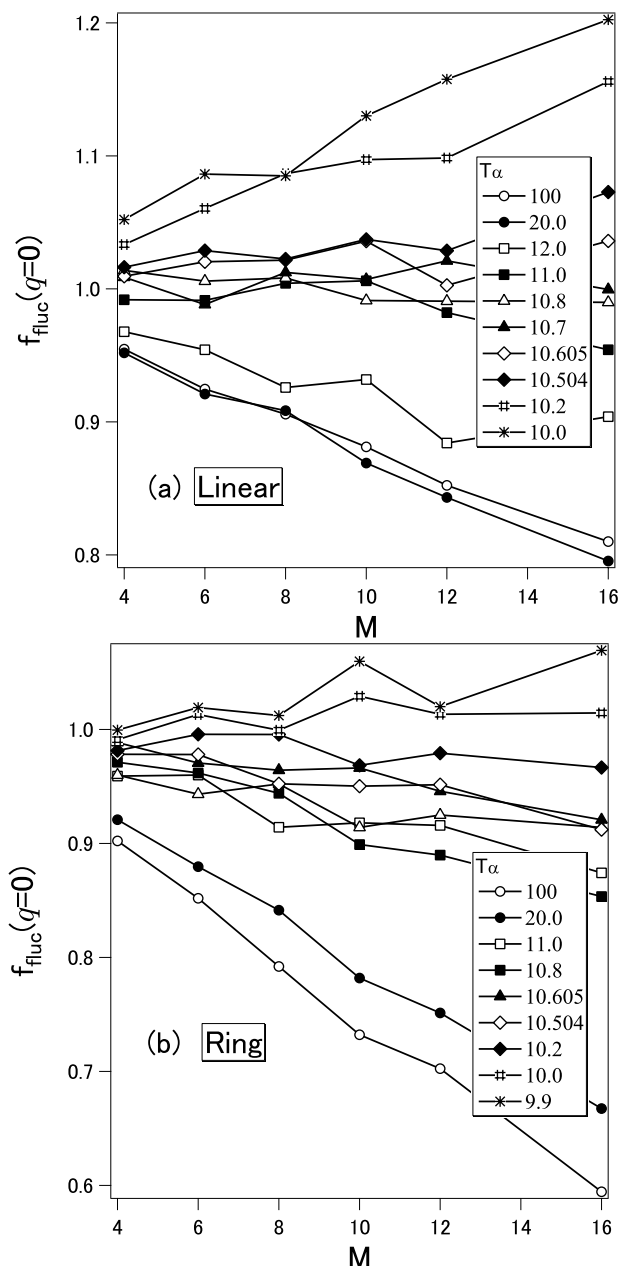


FIG. 7. The scattering intensities at $q=0$, $f_{\text{fluc}}(q=0)$, for each T_α and M for (a) linear and (b) trivial-ring polymers.

distribution functions, a rectangle one for $0 \leq r \leq 100$, and the Gaussian function, $-2 \times 10^{-6} \exp[-(r/100)^2]$, and their scattering functions are calculated numerically and shown in Fig. 6(b). The scattering function for the Gaussian distribution is monotonically increasing one, while that for the rectangle one is damped oscillation function, and their asymptotic values at $q \rightarrow \infty$ are both 1.0. The periodic length of the oscillation function depends on the size of the rectangle. The density functions shown in Fig. 4 are the results for the ensemble averages of the molecular density fluctuated in the solutions. In most experiments, the scattering waves acquired by a detector are the sum of waves scattered from a large number of molecules in a solution, where the periodic length of scattered waves is fluctuated; the oscillation of the scattering waves is suppressed in the summation. Each

scattering function shown in Fig. 5 is fitted with a line in the small q region, $0.07 \leq q \leq 0.12$, by least-squares method. The extrapolated scattering intensities at $q=0$, $f_{\text{fluc}}(q=0)$, are obtained, and the $f_{\text{fluc}}(q=0)$ values vs. M for linear and ring polymers are shown in Fig. 7. The slopes of the curves of $f_{\text{fluc}}(q=0)$ give $2NA_2$, which are increased with decreasing temperatures. This figure clearly shows A_2 is positive at higher T_α , whereas it is negative at lower T_α . Equations (6) and (A7) imply that the $f_{\text{fluc}}(q=0)$ value at $A_2=0$ goes to unity and does not depend on M , meaning that the fluctuation generated by the intermolecular interaction disappears. The C_m value is proportional to M , according to the relationship $C_m = M/(256^3/2)$ [molecules/lattice points].

Fig. 8 compares the $2NA_2$ and 2ν values dependent on the temperature for linear and trivial-ring polymers. It is reasonable that the temperature at $\nu = 1/2$ for linear polymers, $T_\theta(L)$, is identical to the one at $A_2=0$ for linear polymers. The $2NA_2$ values for ring polymers are much larger than those for linear polymers at the same temperature, accordingly, the temperature at $A_2=0$ for ring polymers is evidently lower than that for linear polymers. It is noted that ring polymers have the positive A_2 value at $\nu = 1/2$ and at $T_\alpha = 10.504$, where the trajectory of a ring polymer is statistically described as a closed-random walk; the excluded volume of segments is screened completely by the attractive force between segments in a molecule, but repulsive force between ring polymers remains. Since chain crossings not only in a molecule but also between molecules are inhibited; trivial ring polymers keep their topology, where the topological constraints are working as repulsive forces between polymers, and therefore, the excluded volume effect is emphasized. At $A_2=0$, $T_\alpha = 10.10$, the excluded volumes of ring polymer molecules are screened by the attractive force, where the conformation of a ring polymer chain is shrunk by the attractive force between segments in a molecule and consequently, ν goes smaller than $1/2$.

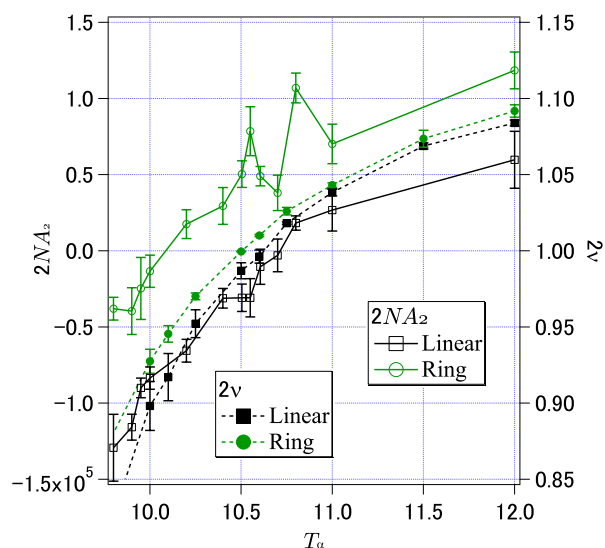


FIG. 8. The temperature dependence of $2NA_2$ and 2ν values for linear and trivial-ring polymers. The 2ν values are the same as those in Fig. 1. The temperature for linear and ring polymers at $A_2=0$ are $T_\alpha = 10.72$ and 10.10 , respectively.

D. Conclusion

A limited but not too small number of polymer molecules, $4 \leq M \leq 16$, were employed, and the A_2 values for linear and trivial ring polymers at various temperatures were calculated based on the molecular density fluctuation in the solution at $N = 1024$. At $T_\theta(L)$, the excluded volumes are screened by the attractive force between segments, where linear polymers can be overlapped with keeping the phantom chain conformation. At $\nu = 1/2$ for trivial ring polymers, the A_2 of ring polymers for intermolecular interaction is positive, where conformations of ring polymers are statistically described as a closed random walk, being their topologies kept. Under this condition, the topological constraints in a trivial ring molecule are working as repulsive force between ring polymers even in dilute condition. R_g value for a ring polymer is much smaller than that for a linear polymer at the same temperature and molecular weight, and hence, interpenetration of a ring polymer chain into neighboring chains is less than a linear chain. This result qualitatively explains the experimental results.²¹⁻²³

ACKNOWLEDGMENTS

The simulation work in this study was executed on the Central Computing System hosted by the Computing Research Center of High Energy Accelerator Research Organization (KEK).

APPENDIX: CALCULATION OF SCATTERING INTENSITY OF POLYMERS IN DILUTE SOLUTION

The number of polymers in the simulation is defined as M . The position vector of center of mass of the j th polymer molecule is \mathbf{r}_j , and the segment density function of the molecule is defined as $\rho_j(\mathbf{r} - \mathbf{r}_j)$. The definition of position vectors is explained in Fig. 9. $\rho(\mathbf{r})$ is the segment density function at \mathbf{r} , which is the sum of each density function, as

$$\rho(\mathbf{r}) = \sum_{j=1}^M \rho_j(\mathbf{r} - \mathbf{r}_j). \quad (\text{A1})$$

\mathbf{q} is a scattering vector, and scattering wave amplitude, $A(\mathbf{q})$, is defined as

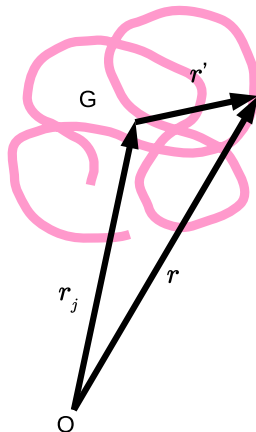


FIG. 9. Definition of position vectors. Points O and G are the origin of the space and the center of mass of the j th molecule, respectively. \mathbf{r}_j is a position vector of G . \mathbf{r} is a position vector in the space and \mathbf{r}' is defined as $\mathbf{r}' = \mathbf{r} - \mathbf{r}_j$.

$$\begin{aligned} A(\mathbf{q}) &= \sum_{j=1}^M \int \rho(\mathbf{r} - \mathbf{r}_j) \exp[-i\mathbf{q} \cdot \mathbf{r}] d\mathbf{r} \\ &= \sum_{j=1}^M \exp[-i\mathbf{q} \cdot \mathbf{r}_j] \int \rho(\mathbf{r}') \exp[-i\mathbf{q} \cdot \mathbf{r}'] d\mathbf{r}' \\ &= \sum_{j=1}^M f(\mathbf{q}) \exp[-i\mathbf{q} \cdot \mathbf{r}_j], \end{aligned} \quad (\text{A2})$$

where $f(\mathbf{q})$ is the structure factor of a molecule. We assume that each polymer molecule in the system has the same $f(\mathbf{q})$, because polymer molecules are in the dilute solutions and $f(\mathbf{q})$ is obtained from the ensemble average of conformations of polymers; $f(\mathbf{q})$ expresses the correlation of the segments in a polymer molecule. Scattering wave intensity, $I(\mathbf{q})$, is the square of the magnitude of $A(\mathbf{q})$,

$$\begin{aligned} I(\mathbf{q}) &= |A(\mathbf{q})|^2 \\ &= \left| \sum_{j=1}^M f(\mathbf{q}) \exp[-i\mathbf{q} \cdot \mathbf{r}_j] \right|^2 \\ &= \sum_{i=1}^M \sum_{j=1}^M f(\mathbf{q})^2 \exp[-i\mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_i)]. \end{aligned} \quad (\text{A3})$$

The terms of $i = j$ in the double summation are separated from the terms of $i \neq j$,

$$\begin{aligned} I(\mathbf{q}) &= M f(\mathbf{q})^2 + \sum_{i \neq j} \exp[-i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)] \\ &= M f(\mathbf{q})^2 + f(\mathbf{q})^2 \sum_i \int_V \rho_i(\mathbf{r}_{ij}) \exp[-i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)] dV_j \\ &= M f(\mathbf{q})^2 \\ &\quad + f(\mathbf{q})^2 \sum_i \int_V (\rho_i(\mathbf{r}_{ij}) - \rho_0) \exp[-i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)] dV_j \\ &\quad + f(\mathbf{q})^2 \sum_i \int_V \rho_0 \exp[-i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)] dV_j, \end{aligned} \quad (\text{A4})$$

where ρ_0 is the averaged density of polymer molecule. $\rho_i(\mathbf{r}_{ij})dV_j$ is the number of polymer molecule at $\mathbf{r}_i - \mathbf{r}_j$ in the volume of dV_j against the polymer molecule at \mathbf{r}_i . The first, second, and third terms in Eq. (A4) show the scattering intensities from a polymer molecule isolated in a dilute solution, from the density fluctuation of polymer molecule against ρ_0 , and from a large body without fluctuation, respectively. The first term in Eq. (A4) can be calculated with a conformation of a polymer molecule. $I_2(\mathbf{q})$ is the second term in Eq. (A4), and can be expressed as,

$$\begin{aligned} I_2(\mathbf{q}) &= f(\mathbf{q})^2 \sum_i \int_V (\rho_i(\mathbf{r}_{ij}) - \rho_0) \exp[-i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)] dV_j \\ &= f(\mathbf{q})^2 M \int_0^R 4\pi r^2 (\rho(r) - \rho_0) \frac{\sin qr}{qr} dr, \end{aligned} \quad (\text{A5})$$

where q is the magnitude of \mathbf{q} . It is assumed in Eq. (A5) that the existing probability of j th polymer molecule against i th polymer is isotropic, and only relies on r . The value of $\rho(r)$ does not include the existing probability of a molecule at $r = 0$, because of the definition of Eq. (A4). If r is large enough, the value of $\rho(r) - \rho_0$ is approached to zero. The

numerical integration in Eq. (A5) can be performed in the range of $0 \leq r \leq R$, where R is larger than the lattice size of the simulator. $I_3(\mathbf{q})$ is the third term in Eq. (A4) and can be transformed to Eq. (A6) with the same method as Eq. (A5) and with the relationship of $M = 4\pi R_3^3 \rho_0 / 3$.

$$\begin{aligned} I_3(\mathbf{q}) &= f(\mathbf{q})^2 \sum_i \int_V \rho_0 \exp[-i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)] dV_j \\ &= f(\mathbf{q})^2 \sum_i \exp[-i\mathbf{q} \cdot \mathbf{r}_i] \int_V \rho_0 \exp[i\mathbf{q} \cdot \mathbf{r}_j] dV_j \\ &= f(\mathbf{q})^2 \rho_0^2 \left(\int_0^{R_3} 4\pi r^2 \frac{\sin qr}{qr} dr \right)^2 \\ &= M f(\mathbf{q})^2 \frac{12\pi \rho_0}{R_3 q^4} \left(\frac{\sin q R_3}{q R_3} - \cos q R_3 \right) \\ &= M f(\mathbf{q})^2 k(q). \end{aligned} \quad (\text{A6})$$

The function of $k(q)$ is a damped oscillated function, where R_3 is the radius of the scattering body which is much larger than the incident wavelength, $\lambda \sim 1/q$. If the value of q is not too small, in the range of $0.1 \leq q$, $R_3 = 1.0 \times 10^5$ and $\rho_0 = 1.0 \times 10^{-3}$, the relationship of $|k(q)| \ll 1$ is obtained. We can safely say that $I_3(\mathbf{q})$ can be ignored, and in general, it means that scattering intensity from a large size of body without fluctuation is zero. Scattering intensity in Eq. (A3) has been transferred into Eq. (A7),^{24–26}

$$\begin{aligned} I(\mathbf{q}) &= M f(\mathbf{q})^2 \left[1 + \int_0^R 4\pi r^2 (\rho(r) - \rho_0) \frac{\sin qr}{qr} dr \right] \\ &= M f(\mathbf{q})^2 f_{\text{fluc}}(q). \end{aligned} \quad (\text{A7})$$

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