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ORIGINAL ARTICLE

Effects of three-segment interactions on the second virial coefficient of ring polymers in the Θ state

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The first-order perturbation calculation is carried out of the second virial coefficient A_2 of the phantom Gaussian and Kratky–Porod (KP) wormlike rings without inter- and intramolecular topological constraints with consideration of the ternary-cluster integral β_3 in addition to the binary-cluster integral β_2. The behavior of the residual contribution of β_3 to A_2 of the KP rings is examined as a function of the reduced total contour length λL as defined as the total contour length L divided by the stiffness parameter λ^{-1}. From a comparison of the present theoretical result with experimental data, it is found that the residual contribution of β_3 to A_2 is negligibly small for ring atactic polystyrene in cyclohexane at Θ in the range of the molecular weight from 1×10^4 to 6×10^5.

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INTRODUCTION

In a previous study,[1] effects of chain stiffness on the second virial coefficient A_2 for *ideal* ring polymers without excluded volume were investigated by Monte Carlo (MC) simulation using a discrete version of the Kratky–Porod (KP) wormlike chain.[2,3] The topological interaction between a pair of ideal rings to keep their linking number Lk zero causes an effective volume V_E excluded to one ring by the presence of another, and therefore makes A_2 (proportional to V_E) positive. The behavior of A_2 was examined as a function of the reduced total contour length λL as defined as the total contour length L of the KP ring divided by the stiffness parameter[3] λ^{-1}. A comparison was also made of the MC results with available literature data[4–6] for ring atactic polystyrene (a-PS) in cyclohexane at Θ (34.5 or 35 °C) in the range of the weight-average molecular weight M_w from 1×10^4 to 6×10^5. Although agreement between the MC and experimental data is fairly well, the former is somewhat (order 10^{-5} $cm^3\,mol\,g^{-2}$) larger than the latter. As the MC values are exact for the ideal KP ring, this minor discrepancy may be regarded as arising from the fact that *real* unperturbed ring polymers in the Θ state cannot fully be described by the ideal KP ring. The purpose of the present study is to consider a possible source of the discrepancy, that is, effects of three-segment interactions on A_2 for the real unperturbed ring polymers.

If the ternary-cluster integral β_3 representing the three-segment interaction is taken into account in addition to the binary-cluster integral β_2 representing the two-segment interaction[7–9] in the perturbation theory[10] of the mean-square end-to-end distance $\langle R^2\rangle$ and A_2, then the first-order perturbation terms in $\langle R^2\rangle$ and A_2 are proportional to the *effective* binary-cluster integral $\beta=\beta_2+\text{const.}\times\beta_3$ in the limit of infinitely large molecular weight M, and the Θ temperature is defined as the temperature at which β but not β_2 vanishes. Note that β_3 is usually positive, so that β_2 is negative at Θ. Strictly, the first-order perturbation term in A_2 has the residual contribution proportional to $-\beta_3 M^{-1/2}$, so that at finite M, A_2 remains small negative (order 10^{-5} $cm^3\,mol\,g^{-2}$) for small M even at Θ. It means that the three-segment contact probability between a pair of linear polymers decreases faster than the two-segment contact probability as M (or λL) is decreased and then the attractive effect due to β_2 (<0) exceeds the repulsive effect due to β_3 (>0). The two effects balance out in the limit of $M\to\infty$. If the situation is also the case with the real unperturbed ring polymer, then the residual contribution seems to make its A_2 smaller than that for the ideal ring.

In practice, we carry out the first-order perturbation calculation of A_2 for the Gaussian and KP rings with consideration of the three-segment interactions in addition to the two-segment ones. In the calculation, we must evaluate an integration of the series expansion of A_2 in terms of the χ function defined by Equation (13.2) of Ref. 10, which corresponds to the Mayer *f*-function,[11] to the first order over the configuration space of a pair of rings under the topological constraint of $Lk=0$. Unfortunately, however, the necessary integrals of the χ function and its triple product for a pair of rings cannot simply be related to β_2 and β_3, respectively, defined for linear chains because of the topological constraint, as explained later in some detail. We then resort to a calculation using a pair of *phantom* rings without the topological constraint in order to utilize β_2 and β_3 also for the ring chains.

MATERIALS AND METHODS

In the first-order perturbation calculation of A_2 for a pair of rings, we take into account the two- and three-segment interactions, the former arising from the contact between two segments (two-body contact) on each of the pair and the latter from that among three segments (three-body contact), two of them on

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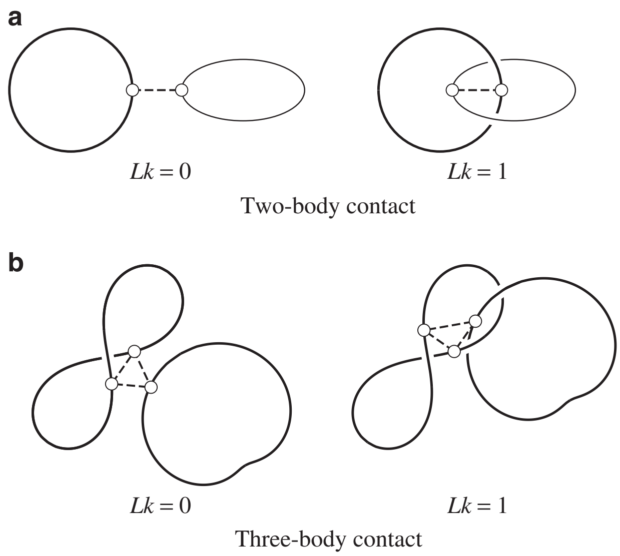

Figure 1 Illustrations of the two-body (**a**) and three-body (**b**) contacts between a pair of rings with $Lk=0$ and 1.

either of the pair and the rest on the other. As easily seen from Figure 1, where the two-body (a) and three-body (b) contacts between a pair of rings with $Lk=0$ and 1 are schematically depicted as examples, the values of the binary- and ternary-cluster integrals resulting from the integrations of the χ function and its triple product, respectively, over the configuration space for the pair of rings with $Lk=0$ are naturally different from those for a pair of linear chains, the latter being obtained by integrations over the full configuration space. Strictly speaking, we must further take account of possible effects of knots. Note that all the rings depicted in Figure 1 are of the trivial knot.

Unfortunately, however, analytical treatment of the inter-[12–15] and intramolecular topological constraints may seem to be impossible even in the case of the Gaussian ring. We therefore adopt *phantom* rings without the constraints in the evaluation of the residual contribution of the ternary-cluster integral to A_2, for convenience, as mentioned above. As a result, we use β_2 and β_3 introduced for the linear chains also for the binary- and ternary-cluster integrals, respectively, for the rings.

Gaussian ring

For the (*phantom*) Gaussian ring composed of n identical beads with the binary- and ternary-cluster integrals β_2 and β_3 connected by the Gaussian bonds with root-mean-square length a, the first-order perturbation theory of A_2 may be given by (see Appendix)

$$A_2 = \frac{N_{\mathrm{A}} n^2}{2M^2}\left[\beta - 6\left(\frac{3}{2\pi a^2}\right)^{3/2}\beta_3 n^{-1} + \cdots\right] \text{(Gaussian ring)}, \tag{1}$$

where N_{A} is the Avogadro constant and β is the effective binary-cluster integral defined by

$$\beta = \beta_2 + 4\left(\frac{3}{2\pi a^2}\right)^{3/2}\beta_3. \tag{2}$$

It is important to note that the definition of β for the Gaussian ring is identical to that for the linear Gaussian chain,[7] and further that the residual contribution, the second term in the square brackets on the right-hand side of Equation (1), is proportional to $n^{-1}\beta_3$ in contrast to the case of the linear Gaussian chain for which the residual contribution is proportional to $n^{-1/2}\beta_3$.[9] The implication is that the relative contributions (or probabilities) of the two- and three-body contacts to A_2 for the Gaussian ring are identical with those for the linear Gaussian chain in the limit of $n\to\infty$ but the residual contributions are different from each other.

Wormlike ring

For the (*phantom*) KP ring of contour length L on which n identical beads with the binary- and ternary-cluster integrals β_2 and β_3 are placed with interval a ($L=na$), the first-order perturbation theory of A_2 may be given by (see Appendix)

$$A_2 = \frac{N_{\mathrm{A}} L^2}{2M^2 a^2}\left\{\beta - 2\left(\frac{3}{2\pi}\right)^{3/2}(\lambda a)^2\left(\frac{\beta_3}{a^3}\right)[I(\infty) - I(\lambda L)] + \cdots\right\} \text{(KP ring)} \tag{3}$$

with λ^{-1} the stiffness parameter and β the effective binary-cluster integral redefined by

$$\beta = \beta_2 + 2\left(\frac{3}{2\pi}\right)^{3/2}(\lambda a)^2\left(\frac{\beta_3}{a^3}\right)I(\infty). \tag{4}$$

The result so obtained for the KP ring is apparently equivalent to that obtained for the linear KP (or HW) chain given by Equation (34) with Equation (35) of Ref. 16 with $c_\infty=1$ except for the expression for the dimensionless function $I(L)$ of (reduced) L which may be given by

$$\begin{aligned} I(L) &= \exp(-16.25L^{-1} + 6.358 - 0.7712L) && \text{for } L\leq 3.075 \\ &= 1.067 - 2.433L^{-1} + 0.01L^{-1}(23.64\Delta^2 - 5.915\Delta^3 \\ &\quad + 0.0009054\Delta^4 - 0.01054\Delta^5) && \text{for } 3.075<L<7.075 \\ &= 1.465 - 3L^{-1} - 30.17L^{-2} + 263.2L^{-3} - 770.1L^{-4} && \text{for } 7.075\leq L \end{aligned} \tag{5}$$

with $\Delta = L-3.075$. The function $I(\lambda L)$ approaches 0 and 1.465 in the limits of $\lambda L\to 0$ and ∞, respectively, as in the case of the linear KP chain,[16] and therefore β defined by Equation (4) becomes identical to that for the linear KP chain. As a result, the factor $I(\infty)-I(\lambda L)$ on the right-hand side of Equation (3) approaches 1.465 and 0 in the limits of $\lambda L\to 0$ and ∞, respectively, as in the case of the linear KP chain, although the asymptotic form $3(\lambda L)^{-1}$ in the limit of $\lambda L\to\infty$ is very different from $4(\lambda L)^{-1/2}$ for the linear KP chain,[16] the situation being consistent with the above-mentioned difference between the linear Gaussian chain and Gaussian ring.

RESULTS AND DISCUSSION

Figure 2 shows plots of $I(\lambda L)-I(\infty)$ against log λL. The heavy solid and dashed curves represent the theoretical values calculated from Equation (5) for the KP ring and from Equation (36) of Ref. 16 for the linear KP chain, respectively. For comparison, in the figure are also plotted values of the asymptotic forms $I(\lambda L)-I(\infty) = -3(\lambda L)^{-1}$ for the KP ring and $I(\lambda L)-I(\infty) = -4(\lambda L)^{-1/2}$ for the linear KP chain, represented by the light solid and dashed curves, respectively, which in principle correspond to the values for the Gaussian ring and linear chain, respectively. It is seen that $I(\lambda L)-I(\infty)$ for the KP ring vanishes with increasing λL more rapidly than that for the linear KP chain because of the above-mentioned difference in the asymptotic form, that is, the former is proportional to $(\lambda L)^{-1}$ while the latter to $(\lambda L)^{-1/2}$.

Now we proceed to we make a comparison of the present theoretical results with the experimental data for ring a-PS in cyclohexane at Θ obtained by Roovers and and Toporowski[4] and by Takano *et al.*[6] For this purpose, we simply assume that A_2 for the KP ring at Θ ($\beta=0$) may be written as a sum of the contribution of the intermolecular topological interaction ($Lk=0$) given by Equation (29) with Equations (25) and (26) in Ref. 1 and the residual contribution of β_3 given by Equation (3) with $\beta=0$ along with Equation (5). On this assumption, the values of A_2 are calculated as a function of M_{w}, λL being converted to M_{w} by log M_{w}=log(λL)+log($\lambda^{-1}M_{\mathrm{L}}$) with M_{L} the shift factor[3] defined as the molecular weight per unit contour length of the KP ring. In the calculation, we use the relation $a=M_0/M_{\mathrm{L}}$, where M_0 is the molecular weight of repeat units and set equal to 104 for a-PS, and the values of the necessary parameters determined for linear

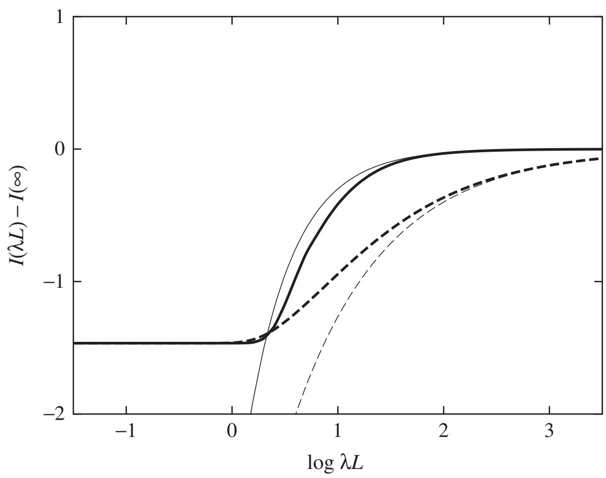

Figure 2 Plots of $I(\lambda L) - I(\infty)$ against log λL. The heavy solid and dashed curves represent the theoretical values calculated from Equation (5) for the KP ring and from Equation (36) of Ref. 16 for the linear KP chain, respectively. The light solid and dashed curves represent the values of the asymptotic forms $I(\lambda L) - I(\infty) = -3(\lambda L)^{-1}$ for the KP ring and $I(\lambda L) - I(\infty) = -4(\lambda L)^{-1/2}$ for the linear KP chain, respectively.

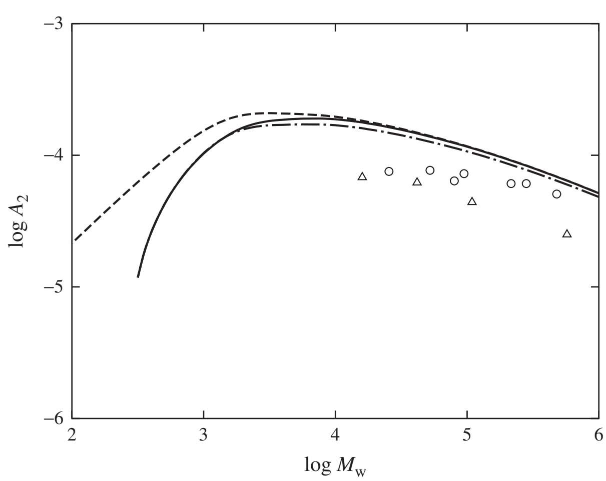

Figure 3 Double-logarithmic plots of A_2 (in cm^3 mol g^{-2}) against M_w. The open circles and triangles represent the experimental values for ring a-PS in cyclohexane at Θ by Roovers and Toporowski[4] with the correction for residual linear a-PS[1] and by Takano *et al.*,[6] respectively. The solid and dashed curves represent the theoretical values for the KP ring with and without the residual contribution of β_3 to A_2. The dot-dashed curve represents the theoretical values for the KP ring with the residual contribution for the linear KP chain.

a-PS in cyclohexane at 34.5 °C (Θ): $\lambda^{-1} = 16.8$ Å,[16] $M_L = 35.8$ Å^{-1},[16] and $\beta_3 = 4.5 \times 10^{-45}$ cm^6.[17] We note that although the ring a-PS samples used in the literatures[4,6] might be of the trivial knot, the difference in A_2 between the ring of the trivial knot and the phantom ring is negligibly small in the range of M where the experimental data exist as shown in figure 6 of Ref. 1.

Figure 3 shows double-logarithmic plots of A_2 (in cm^3 mol g^{-2}) against M_w for ring a-PS in cyclohexane at 34.5 °C (Θ). The open circles and triangles represent the experimental values by Roovers and Toporowski[4] with the correction for residual linear a-PS[1] and by Takano *et al.*,[6] respectively. The solid and dashed curves represent the theoretical values of A_2 at Θ for the KP ring with and without the residual contribution of β_3 to A_2 so calculated. The theoretical values of A_2 with the residual contribution of β_3 deviate downward very slowly from those without the contribution with decreasing M_w, and the deviation is very small in the range of M_w where the experimental data exist. For comparison, there are also plotted the theoretical values for the KP ring with the residual contribution for the linear KP chain, the contribution being calculated from the right-hand side of Equation (34) with $\beta = 0$ along with Equation (36) in Ref. 16 and with the above-mentioned values of λ^{-1}, M_L and β_3 (and M_0), represented by the dot-dashed curve. Although the downward deviation of the values of A_2 with the residual contribution for the linear KP chain from those without the contribution is larger than that in the case of A_2 with the contribution for the KP ring, the theoretical values are still appreciably larger than the experimental ones. It may then be concluded that the consideration of the residual contribution of β_3 cannot compromise the difference between theory and experiment.

CONCLUSION

We have carried out the first-order perturbation calculation of the second virial coefficient A_2 of the phantom Gaussian and KP rings without the intra- and intermolecular topological constraints with consideration of the ternary-cluster integral β_3 in addition to the binary-cluster one β_2. It has been shown that the residual contribution of β_3 to A_2 of the KP rings as a function of the reduced contour length λL increases rapidly from a negative constant and vanishes in the limit of $\lambda L \to \infty$ following the asymptotic relation $A_2 \propto -(\lambda L)^{-1}$ in this limit. From a comparison between the present theoretical results and literature experimental data, it has been found that the residual contribution of β_3 to A_2 is negligibly small for ring a-PS in cyclohexane at Θ in the range of $1 \times 10^4 \lesssim M_w \lesssim 6 \times 10^5$.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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APPENDIX

FIRST-ORDER PERTURBATION THEORY

In this appendix, we derive the first-order perturbation theories of A_2 for the Gaussian and KP rings with consideration of β_3 in addition to β_2.

Gaussian ring

In the same manner as in the case of the first-order perturbation theory of A_2 for the linear Gaussian chain,[7] A_2 for the Gaussian ring under consideration may be expanded in the form

$$A_2 = \frac{N_A n^2}{2M^2}\left[\beta_2 + 2\beta_3 n^{-2}\sum_{i_1=1}^{n-1}\sum_{i_2=i_1+1}^{n}\sum_{i_3=1}^{n} P(\mathbf{0}_{i_1 i_2}) + \cdots\right], \qquad \text{(A1)}$$

where the n beads composing the Gaussian ring are serially numbered 1, 2, $\cdots$, n from an arbitrary bead and $P(\mathbf{0}_{i_1 i_2})$ represents the probability of the contact between the ith and jth beads with $P(\mathbf{R}_{ij})$ being the unperturbed distribution function of the vector distance $\mathbf{R}_{ij}$ between them. The function $P(\mathbf{R}_{ij})$ may be given by[10]

$$P(\mathbf{R}_{ij}) = \left(\frac{3}{2\pi\mu_{ij}a^2}\right)^{3/2}\exp\left(-\frac{3R_{ij}^2}{2\mu_{ij}a^2}\right) \qquad \text{(A2)}$$

with $R_{ij} = |\mathbf{R}_{ij}|$ and $\mu_{ij} = (j-i)[1-(j-i)/n]$. Substitution of Equation (A2) into Equation (A1) and conversion of the sums to integrals leads to

$$A_2 = \frac{N_A n^2}{2M^2}\left\{\beta_2 + 4\left(\frac{3}{2\pi a^2}\right)^{3/2}\beta_3\left[1 - \frac{3}{2}n^{-1} + \mathcal{O}(n^{-2})\right] + \cdots\right\}, \qquad \text{(A3)}$$

where the additional cutoff parameter[9] appearing in the integrations has been set equal to unity as in the case of the linear Gaussian chain.[16] The result may then be rewritten in Equation (1) with Equation (2).

Wormlike ring

In the same manner as in the case of the first-order perturbation theory of A_2 for the linear KP (or HW) chain,[16] A_2 for the KP ring of total contour length L under consideration may be expanded in the form

$$A_2 = \frac{N_A L^2}{2M^2 a^2}\left[\beta_2 + 2\left(\frac{\beta_3}{a^3}\right)\left(\frac{a}{L}\right)^2\int_0^L ds_1\int_{s_1}^L ds_2\int_0^L ds_3 P(\mathbf{0}; s_2 - s_1, L) + \cdots\right] \qquad \text{(A4)}$$

with $P(\mathbf{0};\, s_2 - s_1, L)$ the probability of the contact between the contour points s_1 and s_2 ($0 \le s_1 < s_2 < L$) on the KP ring separated by the contour distance $s_2 - s_1$ (or $L - s_2 + s_1$). In what follows, for simplicity, all lengths are measured in units of λ^{-1} unless otherwise noted, so that, for instance, λL is replaced by (reduced) L. Carrying out the integration in the second term in the square brackets on the right-hand side of Equation (A4) over s_1, s_2 and s_3 with $t = s_2 - s_1$ fixed, we obtain

$$A_2 = \frac{N_A L^2}{2M^2 a^2}\left[\beta_2 + 2\left(\frac{3}{2\pi}\right)^{3/2} a^2\left(\frac{\beta_3}{a^3}\right) I(L) + \cdots\right] \qquad \text{(A5)}$$

with $I(L)$ the dimensionless factor as a function of (reduced) L defined by

$$I(L) = \left(\frac{2\pi}{3}\right)^{3/2}\int_0^L \left(1 - \frac{t}{L}\right) P(\mathbf{0}; t, L)\,dt. \qquad \text{(A6)}$$

Using the relation $P(\mathbf{0}; L-t, L) = P(\mathbf{0}; t, L)$ which naturally holds for the KP ring, Equation (A6) reduces to

$$I(L) = \left(\frac{2\pi}{3}\right)^{3/2}\int_0^{L/2} P(\mathbf{0}; t, L)\,dt. \qquad \text{(A7)}$$

The conditional distribution function $P(\mathbf{R}, \mathbf{u}|\mathbf{u}_0; t, L)$ of both the vector distance $\mathbf{R}$ between the points s_1 and s_2 and the unit tangent vector $\mathbf{u}$ at s_2 with the unit tangent vector $\mathbf{u}_0$ at s_1 fixed may be given by[3,18]

$$P(\mathbf{R}, \mathbf{u}|\mathbf{u}_0; t, L) = [G(\mathbf{0}, \mathbf{u}_0|\mathbf{u}_0; L)]^{-1} G(\mathbf{R}, \mathbf{u}|\mathbf{u}_0; t) G(\mathbf{R}, -\mathbf{u}|-\mathbf{u}_0; L - t), \qquad \text{(A8)}$$

where $G(\mathbf{R}, \mathbf{u}|\mathbf{u}_0; L)$ is the conditional distribution function of the end-to-end vector $\mathbf{R}$ of the linear KP chain of contour length L and the unit tangent vector $\mathbf{u}$ at its terminal end with the unit tangent vector $\mathbf{u}_0$ at its initial end fixed[3] and $G(\mathbf{0}, \mathbf{u}_0|\mathbf{u}_0; L)$ represents the probability that the linear KP chain forms a ring. Integration of both sides of Equation (A8) over $\mathbf{u}$ and $\mathbf{u}_0$ leads to

$$P(\mathbf{0}; t, L) = \frac{1}{4\pi G(\mathbf{0}, \mathbf{u}_0|\mathbf{u}_0; L)}\int G(0, \mathbf{u}|\mathbf{u}_0; t)\, G(\mathbf{0}, \mathbf{u}_0|\mathbf{u}; L - t)\, d\mathbf{u}\, d\mathbf{u}_0, \qquad \text{(A9)}$$

using the relation $G(\mathbf{R}, -\mathbf{u}|-\mathbf{u}_0; L) = G(\mathbf{R}, \mathbf{u}_0|\mathbf{u}; L)$ and the fact that $G(\mathbf{0}, \mathbf{u}_0|\mathbf{u}_0; L)$ is independent of $\mathbf{u}_0$.

The conditional (or angle-dependent) ring-closure probability[3] $G(\mathbf{0}, \mathbf{u}|\mathbf{u}_0; t)$ for the linear KP chain appearing in Equation (A9) may be expanded in terms of the normalized spherical harmonics[3] Y_l^m as follows,[19]

$$G(\mathbf{0}, \mathbf{u}|\mathbf{u}_0; t) = \sum_{l=0}^{\infty} h_l(t)\sum_{m=-l}^{l} Y_l^m(\theta, \phi) Y_l^{m*}(\theta_0, \phi_0), \qquad \text{(A10)}$$

where $h_l(t)$ is the expansion coefficient and $\mathbf{u} = (1, \theta, \phi)$ and $\mathbf{u}_0 = (1, \theta_0, \phi_0)$ in spherical polar coordinates. We note that $h_l(t)$ is identical to $(3/2\pi)^{3/2} g_l(t)/(2l+1)$ with $g_l(t)$ defined in Ref. 19 and also to $h_l^{00}(t)$ given by Equation (8.13) of Ref. 3. For $l=0$ and 1, interpolation formulas for $h_l(t)$ are given by[20]

$$\begin{aligned}
h_0(t) &= 28.01t^{-5}\exp\left(-\frac{7.027}{t}+0.492t\right) && \text{for } 0\le t\le 3.075\\
&= 0.01(4.706-1.844\Delta+0.4185\Delta^2\\
&\quad -0.03791\Delta^3) && \text{for } 3.075<t<7.075\\
&= \left(\frac{3}{2\pi t}\right)^{3/2}\left(1-\frac{5}{8t}\right) && \text{for } 7.075\le t,\\
h_1(t) &= \cos(1.720+0.06104t)\exp(-0.5077t)h_0(t) && \text{for } 0\le t\le 3.075\\
&= 0.01(-6.950+2.322\Delta-0.7346\Delta^2\\
&\quad +0.08655\Delta^3)h_0(t) && \text{for } 3.075<t<7.075\\
&= \left(\frac{3}{2\pi t}\right)^{3/2}\left(-\frac{1}{4t}\right) && \text{for } 7.075\le t
\end{aligned} \tag{A11}$$

with $\Delta=t-3.075$, which have been constructed from the Daniels approximation for large t and a solution for small t with consideration of small thermal fluctuations in the configuration of the KP ring around its most probable one.[21] As for $l\geq 2$, the relation $h_l(t)=\mathcal{O}(t^{-l-3/2})$ for large t can be obtained from Equation (8.13) with Equation (4.177) of Ref. 3 in the Daniels approximation.

Substituting Equation (A10) into Equation (A9) and carrying out the integrations over $\mathbf{u}_0$ and $\mathbf{u}$, we obtain

$$P(\mathbf{0};t,L)=\frac{1}{4\pi G(\mathbf{0},\mathbf{u}_0|\mathbf{u}_0;L)}\sum_{l=0}^{\infty}(2l+1)h_l(t)h_l(L-t). \tag{A12}$$

Substitution of Equation (A12) into Equation (A7) leads to

$$I(L)=\sum_{l=0}^{\infty}I_l(L) \tag{A13}$$

with

$$I_l(L)=\frac{(2\pi/3)^{3/2}(2l+1)}{4\pi G(\mathbf{0},\mathbf{u}_0|\mathbf{u}_0;L)}\int_0^{L/2}h_l(t)h_l(L-t)dt. \tag{A14}$$

In the same manner as in the cases of $h_0(t)$ and $h_1(t)$, an interpolation formula has been constructed for $G(L)=G(\mathbf{0},\mathbf{u}_0\,|\,\mathbf{u}_0;L)$,[21] which is given by

$$\begin{aligned}
G(L) &= \pi^2L^{-6}\exp\left(-\frac{\pi^2}{L}+0.514L\right) && \text{for } L<1.9\\
&= (4\pi)^{-1}(0.03882+0.003494\Delta_1-0.01618\Delta_1^2\\
&\quad +0.008601\Delta_1^3) && \text{for } 1.9<L<2.7\\
&= (4\pi)^{-1}L^{-3/2}(0.3346-0.4810L^{-1}-0.04212L^{-2}\\
&\quad +0.1495L^{-3}) && \text{for } 2.8\lesssim L\lesssim 4\\
&= (4\pi)^{-1}\left(\frac{3}{2\pi L}\right)^{3/2}\left(1-\frac{11}{8L}+\frac{103}{1920L^2}\right) && \text{for } 4\lesssim L
\end{aligned} \tag{A15}$$

with $\Delta_1=L-1.9$.

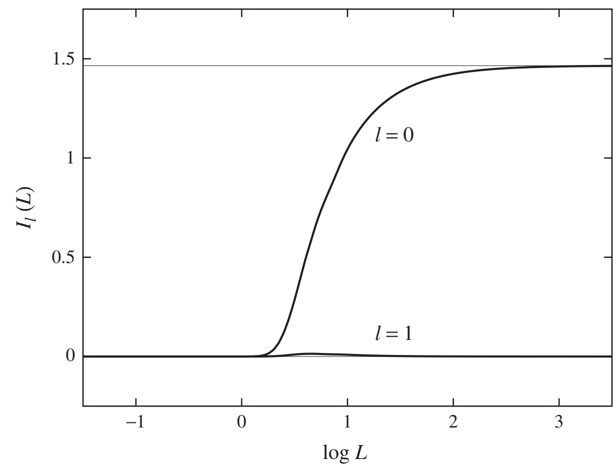

Figure 4 Plots of $I_l(L)$ against log L for $l=0$ and 1. The solid curves represent the theoretical values obtained by numerical integrations of Equation (A14).

From the asymptotic behavior of $h_l(t)h_l(L-t)$ (in the range of $0\leq t\leq L/2$) and $G(L)$ in the limit of $L\to\infty$, it can be shown that $I_l(L)=\mathcal{O}(L^{-l})$ in the limit. We then have

$$I(\infty)=I_0(\infty)=\left(\frac{2\pi}{3}\right)^{3/2}\int_0^{\infty}h_0(t)dt, \tag{A16}$$

where we have used the asymptotic form, $h_0(L-t)/4\pi G(L)=1$, in the limit of $L\to\infty$. Considering the fact that the (angle-independent) ring-closure probability[3] $G(\mathbf{0};t)$ is the integral of $G(\mathbf{0},\mathbf{u}|\mathbf{u}_0;t)$ given by Equation (A10) over $\mathbf{u}$ and therefore identical to $h_0(t)$, $I(\infty)$ for the KP ring is identical to that for the linear KP chain given by Equation (A4) of Ref. 16 with $c_\infty=1$, so that $I(\infty)=1.465$. Although $I(L)$ for the KP ring becomes identical to $I(L)$ for the linear KP chain in the limits of $L\to 0$ and ∞, the behavior of the former as a function of L is different from that of the latter.

Figure 4 shows plots of $I_0(L)$ and $I_1(L)$ against the logarithm of L. It is seen that $I_0(L)$ increases monotonically from 0 to 1.465 with increasing L, while $I_1(L)$ first increases from 0 then decreases to 0 after passing through a very small maximum with increasing L. Since the relative magnitude of $I_1(L)$ to $I_0(L)$ is 2.5% at most, the contributions of $I_l(L)$ with $l\geq 2$ to $I(L)$ may be considered to be very small if any. We therefore put $I(L)\simeq I_0(L)+I_1(L)$ with omission of $I_l(L)$ with $l\geq 2$ in Equation (A13) and construct an interpolation formula for $I(L)$ on the basis of the values of $I_0(L)$ and $I_1(L)$ obtained by numerical integration of the right-hand side of Equation (A14), the formula being given by Equation (5).