Intrinsic Viscosity of Wormlike Regular Three-Arm Stars

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The ratio g_η of the intrinsic viscosity of the Kratky–Porod (KP) wormlike regular three-arm star touched-bead model to that of the KP linear one, both having the same (reduced) total contour length L and (reduced) bead diameter d_b, is numerically evaluated in the Kirkwood–Riseman (KR) approximation. Prior to the evaluation of g_η, an interpolation formula for the mean reciprocal of the end-to-end distance of the once-broken KP chain, which is necessary for the theoretical calculation in the KR approximation, is constructed on the basis of the asymptotic forms derived by the use of the Daniels method near the random-coil limit and the ϵ method near the rod limit and also on the basis of the Monte Carlo results. From an examination of the behavior of g_η as a function of L and d_b, it is found that the ratio g_η/g_η^0 of g_η to the rod-limiting value g_η^0 of g_η monotonically increases from 1 to 2.03 with increasing L and is almost independent of d_b for $d_b \lesssim 0.2$, although the behavior of g_η itself as a function of L remarkably depends on d_b. An empirical interpolation formula is then constructed for g_η/g_η^0 as a function of L, which is considered to be useful for practical purposes.

KEY WORDS: Regular Three-Arm Star Polymer / Intrinsic Viscosity / Semiflexible Polymer / Wormlike Chain / Kirkwood–Riseman Approximation /

In a previous paper,[1] effects of chain stiffness on the ratio g_η of the intrinsic viscosity $[\eta]$ of a regular three-arm star polymer chain to that of the corresponding linear one, both having the same structure and total chain length, have been examined by Monte Carlo (MC) simulation on the basis of the freely rotating chain with the Lennard–Jones 6-12 intramolecular potential between beads. Since there is no theoretical method of obtaining $[\eta]$ without any approximations, we have evaluated it in the three approximate ways: the Kirkwood–Riseman (KR) approximation,[2,3] the Zimm rigid-body ensemble approximation,[4] and the Fixman method.[5,6] We note that upper and lower bounds to $[\eta]$ may be obtained by the Zimm and Fixman methods, respectively, and we have ignored the contribution of the Einstein spheres.[7,8] By combining the two bounds to $[\eta]$ so obtained, we have evaluated upper and lower bounds to g_η and then shown that the KR approximation may give a good approximate g_η value for semiflexible or stiff polymer chains. It is therefore convenient and useful for an analysis of experimental data to construct a theoretical expression for g_η in the KR approximation on the basis of a proper model for semiflexible and stiff polymer chains. The purpose of the present paper is to construct an interpolation formula for g_η of the semiflexible regular three-arm star chain in the KR approximation on the basis of the Kratky–Porod (KP) wormlike chain[7,9] without excluded volume.

For an evaluation of $[\eta]$ for both the KP regular three-arm star and linear chains, we adopt the touched-bead hydrodynamic model so that $[\eta]$ may be written as a sum of the solution $[\eta]_{KR}$ of the KR equation and the contribution $[\eta]_E$ of the Einstein spheres.[7,8] In order to complete the necessary KR equation, *i.e.*, a set of linear simultaneous equations for the hydrodynamic force balance at each bead with the preaveraged Oseen hydrodynamic interaction tensor,[2,3] we need an appropriate approximate expression for the mean reciprocal $\langle R^{-1}\rangle$ of the distance between the centers of two beads, where $\langle\cdots\rangle$ denotes an equilibrium configurational average. Although such an expression is available for a pair of beads on the KP linear chain,[10,11] there are none for a pair of beads on different two arms of the KP star. Prior to the evaluation of $[\eta]$ and g_η, we must therefore derive an approximate expression for $\langle R^{-1}\rangle$ between the two beads on different parts of the once-broken KP chain as a function of the two contour distances from the broken point to the centers of the respective beads. We carry out the task by the use of the two asymptotic methods, *i.e.*, the Daniels method[7,12–14] near the random-coil limit and the ϵ method[7,15,16] near the rod limit, and also of the MC results for the once-broken KP chain.

BASIC EQUATIONS

Consider a regular three-arm star touched-bead model composed of $3m+1$ identical spherical beads of (hydrodynamic) diameter d_b whose centers are located on the KP regular three-arm star chain contour, as illustrated in Figure 1. For convenience, the three arms are designated the first, second, and third ones and the m beads on the ith ($i = 1, 2, 3$) arm are numbered $(i-1)m+1, (i-1)m+2, \ldots, im$ from the branch point (center) to the terminal end, with the center bead numbered 0. The angle between each pair of the unit vectors tangent to the KP contours at the branch point is fixed to be 120°, so that the three vectors are on the same plane. The linear touched-bead model, the counterpart of the above star one, is the KP touched-bead model composed of $n+1$ identical beads of diameter d_b whose centers are located on the KP linear chain contour. We set $n+1$ equal to $3m+1$, so that $n = 3m$. The $n+1$ beads are numbered $0, 1, 2, \ldots, n$ from one end to the other. For both the

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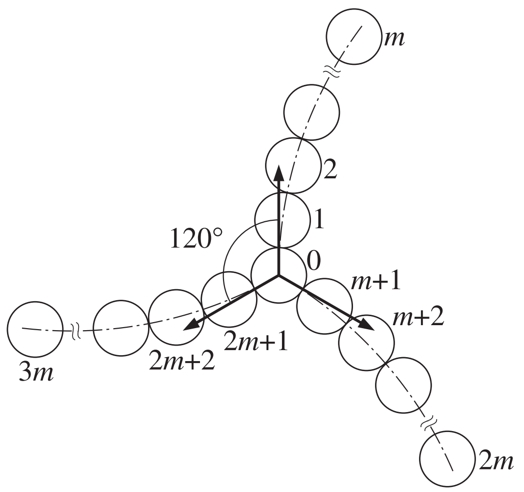

Figure 1. Illustration of the KP regular three-arm star touched-bead model.

star and linear touched-bead models, the contour distance between the two adjacent beads is set equal to d_b.

The intrinsic viscosity [η] of the touched-bead model composed of $n+1$ identical spherical beads of diameter d_b may be written as the sum of the solution $[\eta]_\mathrm{KR}$ of the KR equation and the contribution $[\eta]_\mathrm{E}$ of the Einstein spheres,[7,8] *i.e.*,

$$[\eta] = [\eta]_\mathrm{KR} + [\eta]_\mathrm{E} \tag{1}$$

where

$$[\eta]_\mathrm{KR} = \frac{N_\mathrm{A}}{M}\sum_{i=0}^{n}\phi_{ii} \tag{2}$$

$$[\eta]_\mathrm{E} = \frac{5\pi N_\mathrm{A}(n+1){d_\mathrm{b}}^3}{12M} \tag{3}$$

with N_A the Avogadro constant and M the polymer molecular weight. In eq 2, ϕ_{ij} is the solution of the following linear simultaneous equations,

$$\phi_{ij} + \frac{d_\mathrm{b}}{2}\sum_{\substack{k=0\\ \neq i}}^{n}\langle {R_{ik}}^{-1}\rangle\,\phi_{kj} = \frac{\pi d_\mathrm{b}}{2}\,\langle \mathbf{S}_i\cdot\mathbf{S}_j\rangle \tag{4}$$

where $\langle {R_{ij}}^{-1}\rangle$ is the mean reciprocal of the distance between the centers of the ith and jth beads and $\mathbf{S}_i$ is the vector distance from the center of mass of the chain to the center of the ith bead. In order to complete the KR equation 4, we need an appropriate approximate expression for $\langle {R_{ij}}^{-1}\rangle$ along with the theoretical expression for the equilibrium average $\langle \mathbf{S}_i\cdot\mathbf{S}_j\rangle$. We first give the latter and then consider the former. In what follows, all lengths are measured in units of the stiffness parameter λ^{-1} of the KP chain unless otherwise specified.

AVERAGE $\langle \mathbf{S}_i\cdot\mathbf{S}_j\rangle$

As in the previous study of [η] of the linear touched-bead model,[8] where we have adopted the value of $\langle \mathbf{S}_i\cdot\mathbf{S}_j\rangle$ of the (continuous) KP chain of total contour length $L=(n+1)d_\mathrm{b}$ as that of the (discrete) touched-bead model, we adopt the value of $\langle \mathbf{S}_i\cdot\mathbf{S}_j\rangle$ of the KP regular three-arm star chain of total contour length $L=(3m+1)d_\mathrm{b}$ as that of the regular three-arm star touched-bead model. Here, L has consistently been set equal to the total number $n+1$ or $3m+1$ of beads multiplied by d_b for both the linear and star chains. The relation $L=(3m+1)d_\mathrm{b}$ leads to the relation $L_\mathrm{a}=(m+\frac{1}{3})d_\mathrm{b}$ between the contour length $L_\mathrm{a}=\frac{1}{3}L$ of each arm and d_b. Although the latter relation seems somewhat awkward because of the inclusion of the non-integer term $\frac{1}{3}$, it only reflects the fact that the center bead belongs to all the three arms.

For the $[(i-1)m+k]$th and $[(j-1)m+l]$th beads ($i, j = 1,2,3;\ k,\ l=1,2,\ldots,m$) of the regular three-arm star chain, *i.e.*, the kth bead on the ith arm and the lth bead on the jth arm, respectively, $\langle \mathbf{S}_{(i-1)m+k}\cdot\mathbf{S}_{(j-1)m+l}\rangle$ may then be given by

$$\langle \mathbf{S}_{(i-1)m+k}\cdot\mathbf{S}_{(j-1)m+l}\rangle = \langle \mathbf{S}(t_k^{(i)})\cdot\mathbf{S}(t_l^{(j)})\rangle \tag{5}$$

where $\mathbf{S}(t_k^{(i)})$ is the vector distance from the center of mass of the KP regular three-arm star chain to the contour point on the ith arm with the contour distance $t_k^{(i)}$ from the branch point, so that

$$t_k^{(i)} = k d_\mathrm{b} \tag{6}$$

The average $\langle \mathbf{S}(t_k^{(i)})\cdot\mathbf{S}(t_l^{(j)})\rangle$ may be given by (see APPENDIX A)

$$\begin{aligned}\langle \mathbf{S}(t_k^{(i)})\cdot\mathbf{S}(t_l^{(j)})\rangle = {} & \frac{L}{27} + \frac{(t_k^{(i)})^2+(t_l^{(j)})^2}{2L} + \frac{t_k^{(i)}+t_l^{(j)}}{6} - \frac{u_{kl}^{(ij)}}{2}\\ & + \frac{1}{24}(1-3\delta_{ij})[1-\exp(-2t_k^{(i)})\\ & - \exp(-2t_l^{(j)})] - \frac{1}{8}(1+\delta_{ij})\exp(-2u_{kl}^{(ij)})\\ & + \frac{1}{4L} - \frac{1}{4L}e^{-2L/3}[\cosh(2t_k^{(i)})+\cosh(2t_l^{(j)})]\\ & + \frac{3}{16L^2}(1-e^{-4L/3})\end{aligned} \tag{7}$$

where δ_{ij} is the Kronecker delta and $u_{kl}^{(ij)}$ is defined by

$$u_{kl}^{(ij)} = [(t_k^{(i)})^2 + (t_l^{(j)})^2 + 2(1-2\delta_{ij})t_k^{(i)}t_l^{(j)}]^{1/2} \tag{8}$$

We note that $\langle \mathbf{S}_{(i-1)m+k}\cdot\mathbf{S}_0\rangle = \langle \mathbf{S}(t_k^{(i)})\cdot\mathbf{S}(0)\rangle$ and $\langle \mathbf{S}_0\cdot\mathbf{S}_0\rangle = \langle \mathbf{S}(0)\cdot\mathbf{S}(0)\rangle$ are also given by eq 7 with $u_{kl}^{(ij)} = t_k^{(i)}$ and 0, respectively. In the rod limit, *i.e.*, the limit of L (in units of λ^{-1}) $\to 0$, eq 7 reduces to

$$\langle \mathbf{S}(t_k^{(i)})\cdot\mathbf{S}(t_l^{(j)})\rangle = \frac{1}{2}(3\delta_{ij}-1)t_k^{(i)}t_l^{(j)} \quad \text{(rod limit)} \tag{9}$$

As for the linear touched-bead model, $\langle \mathbf{S}_i\cdot\mathbf{S}_j\rangle$ ($i, j = 0,1,2,\ldots,n$) may be given by

$$\langle \mathbf{S}_i\cdot\mathbf{S}_j\rangle = \langle \mathbf{S}(t_i)\cdot\mathbf{S}(t_j)\rangle \tag{10}$$

where $\mathbf{S}(t_i)$ is the vector distance from the center of mass of the KP linear chain to its contour point with the contour distance t_i from one end, so that

$$t_i = \left(i+\frac{1}{2}\right)d_\mathrm{b} \tag{11}$$

The average $\langle \mathbf{S}(t)\cdot\mathbf{S}(t')\rangle$ is given by eq 19 in ref 17 and may be written in the form,

$$\langle \mathbf{S}(t)\cdot\mathbf{S}(t')\rangle = \frac{L}{3} + \frac{t^2+t'^2}{2L} - \frac{t+t'}{2} - \frac{|t-t'|}{2} - \frac{e^{-2|t-t'|}}{4} + \frac{1}{8L}[2-e^{-2t}-e^{-2t'}-e^{-2(L-t)}-e^{-2(L-t')}] + \frac{1}{8L^2}(1-e^{-2L}) \quad (12)$$

In the rod limit, it reduces to

$$\langle \mathbf{S}(t)\cdot\mathbf{S}(t')\rangle = \frac{1}{4}(2t-L)(2t'-L) \quad \text{(rod limit)} \quad (13)$$

MEAN RECIPROCAL OF THE END-TO-END DISTANCE

The mean reciprocal $\langle R_{[(i-1)m+k][(j-1)m+l]}{}^{-1}\rangle$ of the distance $R_{[(i-1)m+k][(j-1)m+l]}$ between the centers of the kth bead on the ith arm and lth bead on the jth arm may be given by

$$\langle R_{[(i-1)m+k][(j-1)m+l]}{}^{-1}\rangle = \langle R^{-1}(t_k^{(i)}, t_l^{(j)})\rangle \quad (14)$$

where $\langle R^{-1}(t_k^{(i)}, t_l^{(j)})\rangle$ is the mean reciprocal of the distance between the contour points $t_k^{(i)}$ and $t_l^{(j)}$ on the KP regular three-arm star chain.

We first consider asymptotic forms for the mean reciprocal $\langle R^{-1}(t_1, t_2, \theta)\rangle$ of the end-to-end distance of the once-broken KP chain of total contour length $t_1 + t_2$ such that two KP subchains 1 and 2 of contour lengths t_1 and t_2, respectively, are connected with a bending angle θ, *i.e.*, the angle between the unit vectors $\mathbf{u}_1$ and $\mathbf{u}_2$ tangent to the contours of the subchains 1 and 2, respectively, at the broken point, as illustrated in Figure 2. We then construct an interpolation formula for the case of $\theta = 120°$ on the basis of the asymptotic forms so obtained and also of MC results for the once broken KP chain.

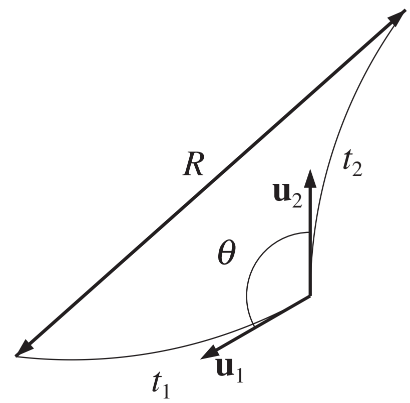

Figure 2. Illustration of the once-broken KP chain.

Asymptotic Forms

The asymptotic forms for $\langle R^{-1}(t_1, t_2, \theta)\rangle$ in the cases of $t_1 \gg 1$ and $t_2 \gg 1$, $t_1 \gg 1$ and $t_2 \ll 1$, $t_1 \ll 1$ and $t_2 \gg 1$, and $t_1 \ll 1$ and $t_2 \ll 1$ may be written in the form (see APPENDIX B),

$$\begin{aligned}\langle R^{-1}(t_1,t_2,\theta)\rangle &= \langle R^2\rangle^{-1/2} f_{\mathrm{DD}}(t_1,t_2,\theta) \quad \text{for } t_1 \gg 1, t_2 \gg 1\\ &= \langle R^2\rangle^{-1/2} f_{\mathrm{D}\epsilon}(t_1,t_2,\theta) \quad \text{for } t_1 \gg 1, t_2 \ll 1\\ &= \langle R^2\rangle^{-1/2} f_{\epsilon\mathrm{D}}(t_1,t_2,\theta) \quad \text{for } t_1 \ll 1, t_2 \gg 1\\ &= \langle R^2\rangle^{-1/2} f_{\epsilon\epsilon}(t_1,t_2,\theta) \quad \text{for } t_1 \ll 1, t_2 \ll 1\end{aligned} \quad (15)$$

where

$$f_{\mathrm{DD}}(t_1,t_2,\theta) = \left(\frac{6}{\pi}\right)^{1/2}\left\{1 - \frac{11}{40\langle R^2\rangle} + \frac{1}{80\langle R^2\rangle^2}\left[\frac{431}{56} + 11(1+\cos\theta) + \frac{11}{2}(1-\cos^2\theta)\right]\right\} \quad (16)$$

$$f_{\mathrm{D}\epsilon}(t_1,t_2,\theta) = \left(\frac{6}{\pi}\right)^{1/2}\left\{1 - \frac{11}{40\langle R^2\rangle} + \frac{1}{40\langle R^2\rangle^2}\left[\frac{431}{112} + 9{t_2}^2(1-\cos^2\theta)\right]\right\} \quad (17)$$

$$f_{\epsilon\epsilon}(t_1,t_2,\theta) = 1 + \frac{3}{8}\left(\frac{\langle R^4\rangle}{\langle R^2\rangle^2} - 1\right) \quad (18)$$

and $f_{\epsilon\mathrm{D}}(t_1,t_2,\theta) = f_{\mathrm{D}\epsilon}(t_2,t_1,\theta)$. In eqs 15–18, $\langle R^2\rangle = \langle R^2(t_1,t_2,\theta)\rangle$ and $\langle R^4\rangle = \langle R^4(t_1,t_2,\theta)\rangle$ are the second and fourth moments, respectively, of the end-to-end distance of the once-broken KP chain given by

$$\langle R^2(t_1,t_2,\theta)\rangle = t_1 + t_2 - \frac{1}{2}[1-e^{-2(t_1+t_2)}] - \frac{1}{2}(1-e^{-2t_1})(1-e^{-2t_2})(1+\cos\theta) \quad (19)$$

$$\begin{aligned}\langle R^4(t_1,t_2,\theta)\rangle &= \frac{5}{3}(t_1+t_2)^2 - (t_1+t_2)\left[\frac{26}{9} + e^{-2(t_1+t_2)}\right] + 2[1-e^{-2(t_1+t_2)}] - \frac{1}{54}[1-e^{-6(t_1+t_2)}]\\ &\quad - \left\{(1-e^{-2t_1})\left[\frac{5}{3}t_2 + t_2e^{-2t_2} - \frac{3}{2}(1-e^{-2t_2}) + \frac{1}{18}(1-e^{-6t_2})\right]\right.\\ &\quad \left. + (1-e^{-2t_2})\left[\frac{5}{3}t_1 + t_1e^{-2t_1} - \frac{3}{2}(1-e^{-2t_1}) + \frac{1}{18}(1-e^{-6t_1})\right]\right\}(1+\cos\theta)\\ &\quad - \frac{1}{4}\left[(1-e^{-2t_1}) - \frac{1}{3}(1-e^{-6t_1})\right]\left[(1-e^{-2t_2}) - \frac{1}{3}(1-e^{-6t_2})\right](1-\cos^2\theta)\end{aligned} \quad (20)$$

We note that $f_{D\epsilon}(t, 0, \theta)$ given by eq 17 with $t_1 = t$ and $t_2 = 0$ [or $f_{\epsilon D}(0, t, \theta)$] is identical with the second Daniels approximate expression for the mean reciprocal of the end-to-end distance of the KP linear chain of total contour length t obtained by Yamakawa and Fujii,[11] up to $\mathcal{O}(t^{-2})$, and also note that the expression for $\langle R^2(t_1, t_2, \theta)\rangle$ given by eq 19 was first derived by Mansfield and Stockmayer.[18] In the rod limit, eq 15 (strictly the fourth equation) reduces to

$$\langle R^{-1}(t_1, t_2, \theta)\rangle = [R_{\mathrm{rod}}(t_1, t_2, \theta)]^{-1} \quad \text{(rod limit)} \tag{21}$$

where $R_{\mathrm{rod}}(t_1, t_2, \theta)$ is the end-to-end distance of the once-broken rod composed of the two straight rods of lengths t_1 and t_2 with the bending angle θ and is given by

$$R_{\mathrm{rod}}(t_1, t_2, \theta) = ({t_1}^2 + {t_2}^2 - 2t_1t_2\cos\theta)^{1/2} \tag{22}$$

Figures 3, 4, and 5 show plots of $R_{\mathrm{rod}}(t_1, t_2, 120°)\langle R^{-1}(t_1, t_2, 120°)\rangle$ against t_1 for the once-broken KP chain with $\theta = 120°$ and with $t_2 = 0.1$, 1, and 2, respectively. The dashed (DD), two dot-dashed (Dϵ and ϵD), and dotted ($\epsilon\epsilon$) curves represent the theoretical asymptotic values calculated from eq 15 with eqs 16, 17, and 18, respectively, with $\theta = 120°$. In the figures, the unfilled circles and the solid curves represent the MC values and those calculated from an interpolation formula, which are obtained in the following two subsections.

MC Simulation

As seen from Figures 3, 4, and 5, it is difficult to construct an interpolation formula on the basis only of the theoretical asymptotic values because they cannot cover the whole range of t_1. In order to obtain additional reference values of $\langle R^{-1}(t_1, t_2, 120°)\rangle$, we carry out MC simulation by the use of the ideal once-broken freely rotating chain such that two freely rotating subchains 1 and 2 are connected with a bending angle 120°, the subchain i ($i = 1, 2$) being composed of n_i bonds of length a (in units of λ^{-1}) joined with a complementary bond angle α. We note that the subchain i becomes identical with the KP chain of total contour length t_i in the limit of $n_i \to \infty$ and $a \to 0$ under the conditions $t_i = n_i a$ and $1 - \cos\alpha = 2a$. As done by Yamakawa and Fujii,[11] we replace the KP subchains approximately by the freely rotating ones having very small but finite α satisfying the above two conditions, *i.e.*, $a = 0.01$ and $\cos\alpha = 0.98$.

By the use of the once-broken freely rotating chain so defined, we evaluate $\langle R^{-1}(t_1, t_2, 120°)\rangle$ as follows. Let $\mathbf{a}_k^{(i)}$ ($i = 1, 2$; $k = 1, 2, \ldots, n_i$) be the kth bond vector on the subchain i, the bond vectors being numbered $1, 2, \ldots, n_i$ from the broken point to the end of the subchain i, and let $\mathbf{a}_1^{(1)} = (0, 0, a)^T$ and $\mathbf{a}_1^{(2)} = (\sqrt{3}a/2, 0, -a/2)^T$ in an external Cartesian coordinate system with the superscript T indicating the transpose. In the

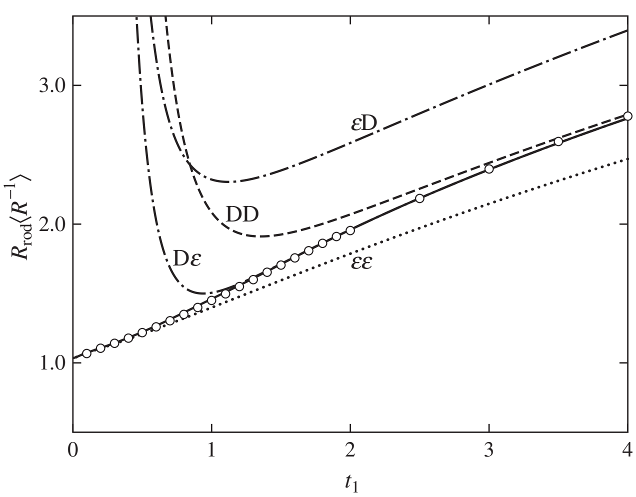

Figure 3. Plots of $R_{\mathrm{rod}}(t_1, t_2, 120°)\langle R^{-1}(t_1, t_2, 120°)\rangle$ against t_1 for the once-broken KP chain with $\theta = 120°$ and $t_2 = 0.1$. The unfilled circles represent the MC values. The solid curve represents the values of the interpolation formula and the dashed (DD), two dot-dashed (Dϵ and ϵD), and dotted ($\epsilon\epsilon$) curves represent the theoretical asymptotic values for $t_1 \gg 1$ and $t_2 \gg 1$, $t_1 \gg 1$ and $t_2 \ll 1$, $t_1 \ll 1$ and $t_2 \gg 1$, and $t_1 \ll 1$ and $t_2 \ll 1$, respectively (see the text).

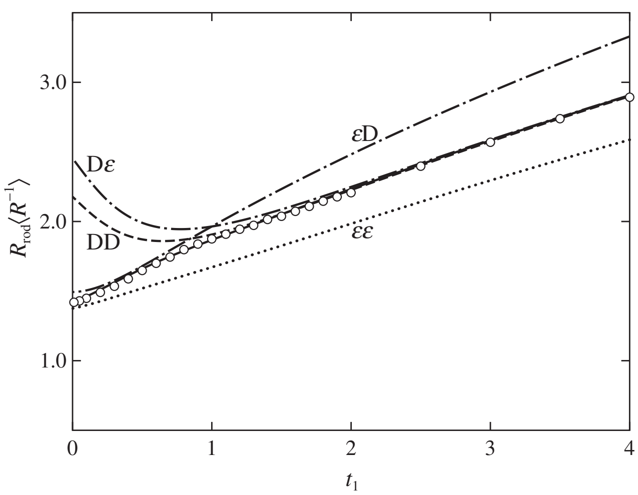

Figure 4. Plots of $R_{\mathrm{rod}}(t_1, t_2, 120°)\langle R^{-1}(t_1, t_2, 120°)\rangle$ against t_1 for the once-broken KP chain with $\theta = 120°$ and $t_2 = 1$. All the symbols and curves have the same meaning as those in Figure 3.

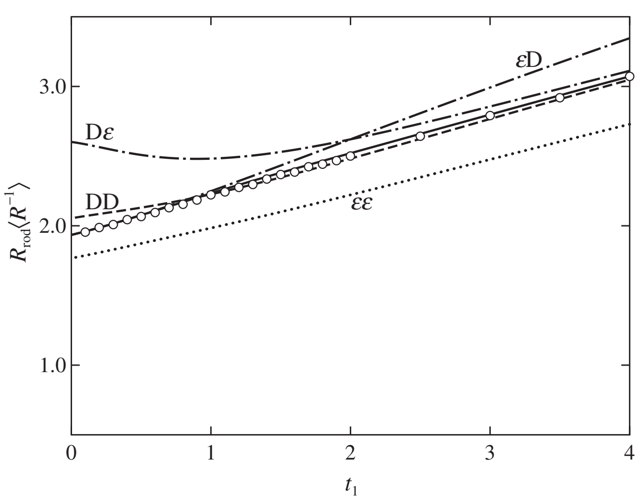

Figure 5. Plots of $R_{\mathrm{rod}}(t_1, t_2, 120°)\langle R^{-1}(t_1, t_2, 120°)\rangle$ against t_1 for the once-broken KP chain with $\theta = 120°$ and $t_2 = 2$. All the symbols and curves have the same meaning as those in Figure 3.

external system, $\mathbf{a}_k^{(i)}$ may then be written in the form,

$$\begin{aligned}\mathbf{a}_k^{(i)} = {} & [\mathbf{A}(120^\circ, 180^\circ)]^{i-1} \cdot \mathbf{A}(\alpha, \phi_1^{(i)}) \cdot \mathbf{A}(\alpha, \phi_2^{(i)}) \cdots \\ & \mathbf{A}(\alpha, \phi_{k-1}^{(i)}) \cdot (0, 0, a)^T\end{aligned} \tag{23}$$

where $\phi_k^{(i)}$ is the internal rotation angle around $\mathbf{a}_k^{(i)}$ and $\mathbf{A}(\alpha, \phi)$ is the orthogonal transformation matrix defined by

$$\mathbf{A}(\alpha, \phi) = \begin{pmatrix} -\cos\alpha\cos\phi & \sin\phi & -\sin\alpha\cos\phi \\ -\cos\alpha\sin\phi & -\cos\phi & -\sin\alpha\sin\phi \\ -\sin\alpha & 0 & \cos\alpha \end{pmatrix} \tag{24}$$

The configuration of the once-broken freely rotating chain may therefore be specified by the set of $n_1 + n_2 - 2$ internal rotation angles $\{\phi_{n_1+n_2-2}\} = (\phi_1^{(1)}, \phi_2^{(1)}, \ldots, \phi_{n_1-1}^{(1)}, \phi_1^{(2)}, \phi_2^{(2)}, \ldots, \phi_{n_2-1}^{(2)})$. On the basis of N sample configurations, *i.e.*, N sets of $n_1 + n_2 - 2$ internal rotation angles randomly chosen in the interval $[-\pi, \pi]$, $\langle R^{-1}(t_1, t_2, 120^\circ)\rangle$ may be evaluated from

$$\langle R^{-1}(t_1, t_2, 120^\circ)\rangle = N^{-1} \sum_{\{\phi_{n_1+n_2-2}\}} \left| \sum_{i=1}^{n_1} \mathbf{a}_i^{(1)} - \sum_{j=1}^{n_2} \mathbf{a}_j^{(2)} \right|^{-1} \tag{25}$$

where the first sum is taken over the N sample configurations.

In practice, we have adopted $N = 10^5$. All the numerical work has been done by the use of a personal computer with an Intel Pentium4 CPU with a clock rate of 3.00 GHz. A source program coded in C has been compiled by the GNU C compiler version 3.3.3 with real variables of double precision.

The MC values of $R_{\text{rod}}(t_1, t_2, 120^\circ)\langle R^{-1}(t_1, t_2, 120^\circ)\rangle$ so obtained for $t_2 = 0.1$, 1, and 2 are also shown in Figures 3, 4, and 5, respectively (unfilled circles). It is seen from Figure 3 for the case of small t_2 $(= 0.1)$ that the MC values connect smoothly the $\epsilon\epsilon$ values which are valid for $t_1 \ll 1$ and $t_2 \ll 1$ and the Dϵ ones which are valid for $t_1 \gg 1$ and $t_2 \ll 1$. In the case of large t_2 $(= 2)$, on the other hand, it is seen from Figure 5 that the MC values connect smoothly the ϵD values which are valid for $t_1 \ll 1$ and $t_2 \gg 1$ and the DD ones which are valid for $t_1 \gg 1$ and $t_2 \gg 1$. In the case of intermediate t_2 $(= 1)$ shown in Figure 4, The MC values lie between the $\epsilon\epsilon$ and ϵD values for $t_1 \lesssim 1$ and follow the DD values for $t_1 \gtrsim 1$.

Interpolation Formula

Now we are in a position to construct an interpolation formula for $\langle R^{-1}(t_1, t_2, 120^\circ)\rangle$ on the basis of the theoretical asymptotic forms given by eqs 15 with eqs 16–18 along with the MC ones for the once-broken KP chain.

The asymptotic form $f_{\text{D}\epsilon}$ (or $f_{\epsilon\text{D}}$) is not symmetric with respect to the pair of variables t_1 and t_2 and is not convenient for further developments as it stands. We therefore construct a hybrid $f_{\text{DD}\epsilon}(t_1, t_2, 120^\circ)$ between $f_{\text{DD}}(t_1, t_2, 120^\circ)$ and $f_{\text{D}\epsilon}(t_1, t_2, 120^\circ)$ given by eqs 16 and 17, respectively, both with $\theta = 120^\circ$, prior to the construction of the interpolation formula, which may be written in the form,

$$\begin{aligned}& f_{\text{DD}\epsilon}(t_1, t_2, 120^\circ) \\ & = \left(\frac{6}{\pi}\right)^{1/2} \left[1 - \frac{11}{40\langle R^2\rangle} + \frac{431}{4480\langle R^2\rangle^2} + \frac{C(t_1, t_2)}{\langle R^2\rangle^2}\right]\end{aligned} \tag{26}$$

where $C(t_1, t_2)$ is given by

$$C(t_1, t_2) = \frac{108\bar{t}^2 + 77\bar{t}^4}{640(1 + \bar{t}^4)} \tag{27}$$

with

$$\bar{t}^2 = (t_1^{-2} + t_2^{-2})^{-1} \tag{28}$$

We note that $f_{\text{DD}\epsilon}$ so defined has the symmetry relation $f_{\text{DD}\epsilon}(t_1, t_2, 120^\circ) = f_{\text{DD}\epsilon}(t_2, t_1, 120^\circ)$ and recovers f_{DD} given by eq 16 up to $\mathcal{O}(t_2{}^{-2})$ in the case of $t_2 \gg 1$ and $f_{\text{D}\epsilon}$ given by eq 17 up to $\mathcal{O}(t_2{}^2)$ in the case of $t_2 \ll 1$.

By combining $f_{\epsilon\epsilon}$ and $f_{\text{DD}\epsilon}$ given by eqs 18 and 26, respectively, we then assume that $\langle R^{-1}(t_1, t_2, 120^\circ)\rangle$ may be well represented by the following interpolation formula,

$$\begin{aligned}& \langle R^{-1}(t_1, t_2, 120^\circ)\rangle \\ & = \langle R^2\rangle^{-1/2}\big[1 + A_1\langle R^2\rangle^{A_2}\big]^{-1}[f_{\epsilon\epsilon}(t_1, t_2, 120^\circ) + A_3\langle R^2\rangle^{3/2} \\ & \quad + A_4 t_1 t_2 (t_1 + t_2) e^{-A_5 t_1 t_2} + A_1\langle R^2\rangle^{A_2} f_{\text{DD}\epsilon}(t_1, t_2, 120^\circ)]\end{aligned} \tag{29}$$

where $\langle R^2\rangle = \langle R^2(t_1, t_2, 120^\circ)\rangle$ is given by eq 19 with $\theta = 120^\circ$. In eq 29, $A_1, A_2, \ldots, A_5$ are numerical constants which must be determined so that the interpolation formula may well reproduce the MC values evaluated in the last subsection, their optimum values being given by

$$A_1 = 5, \quad A_2 = \frac{11}{2}, \quad A_3 = 0.045, \quad A_4 = 0.40, \quad A_5 = 1 \tag{30}$$

In Figures 3–5, the solid curves represent the approximate values calculated from eq 29 with eqs 18–20, 26–28, and 30 with $\theta = 120^\circ$. It is seen that the interpolation formula so constructed may well reproduce the MC values.

Finally, the necessary $\langle R_{[(i-1)m+k][(j-1)m+l]}{}^{-1}\rangle$ may be given by eq 14 with $\langle R^{-1}(t_k^{(i)}, t_l^{(j)})\rangle$ given by

$$\begin{aligned}\langle R^{-1}(t_k^{(i)}, t_l^{(j)})\rangle &= \langle R^{-1}(t_k^{(i)}, t_l^{(j)}, 120^\circ)\rangle \qquad \text{for } i \neq j \\ &= \langle R^{-1}(|t_k^{(i)} - t_l^{(i)}|, 0, 120^\circ)\rangle \quad \text{for } i = j\end{aligned} \tag{31}$$

We note that $\langle R^{-1}(t, 0, 120^\circ)\rangle$ and/or $\langle R^{-1}(0, t, 120^\circ)\rangle$ represent the mean reciprocal of the end-to-end distance of the KP linear chain of total contour length t and its approximate value calculated from eq 29 with eqs 18–20, 26–28, and 30 and with $t_1 = t$ and $t_2 = 0$ agrees with that calculated from the Yamakawa–Fujii[11] interpolation formula for the KP linear cylinder (with the cylinder diameter $d = 0$) within 0.7% over the whole range of t.

RESULTS FOR g_η FACTOR

We have calculated the KR contribution $[\eta]_{\text{KR}}$ to the intrinsic viscosity $[\eta]$ from eq 2 with the numerical solutions ϕ_{ii} of the linear simultaneous equations 4 for both the KP regular three-arm star and linear touched-bead models, in the ranges of the total number $n + 1$ of beads from 4 to 1501 and of the bead diameter d_{b} from 0.001 to 0.4. Note that the total contour length L of the chain is equal to $(n + 1)d_{\text{b}}$, as already mentioned. In eq 4, $\langle R^{-1}(t_k^{(i)}, t_l^{(j)})\rangle$ is given by eq 31 with eqs 18–20 and 26–30 for the star chain and by the second of

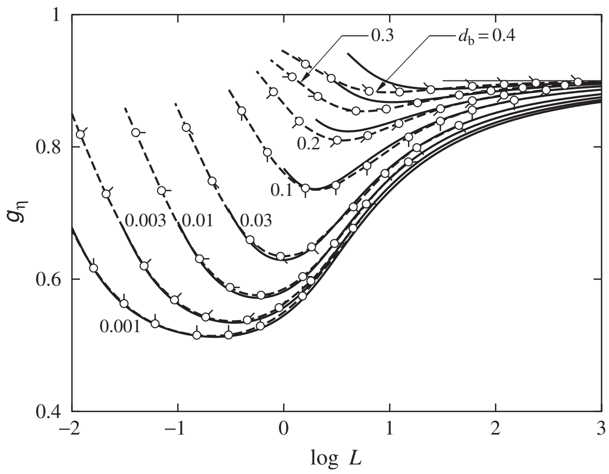

Figure 6. Plots of $g_\eta(L, d_b)$ against $\log L$. The unfilled circles represent the theoretical values, various directions of pips indicating different values of d_b indicated. The dashed curves connect smoothly the theoretical values at constant d_b. The horizontal line segment indicates the value 0.90 obtained by Irurzun[19] for the Gaussian regular three-arm star chain. The solid curves represent the values calculated from the interpolation formula (see the text).

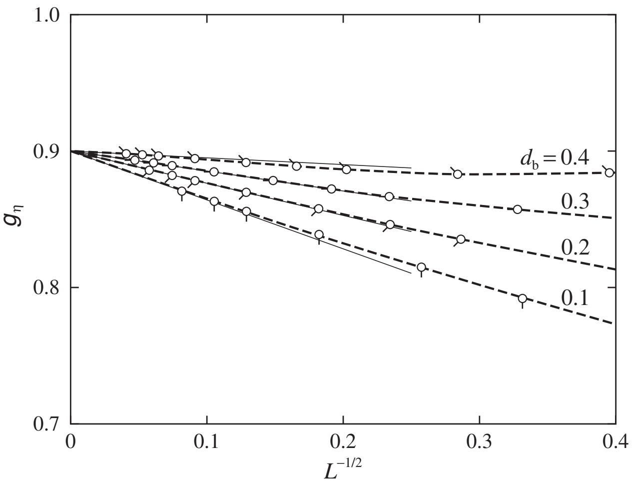

Figure 7. Plots of $g_\eta(L, d_b)$ against $L^{-1/2}$. All the symbols have the same meaning as those in Figure 6. The dashed curves connect smoothly the theoretical values at constant d_b and the solid straight lines indicate the respective initial tangents.

eq 31 for the linear one and $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ is given by eq 7 with eq 8 for the former and by eq 12 for the latter. We then have calculated [η] from eq 1 with the values of $[\eta]_{\mathrm{KR}}$ so obtained along with $[\eta]_{\mathrm{E}}$ calculated from eq 3, for both the star and linear chains. Finally we have evaluated g_η as a function of L and d_b from the defining equation,

$$g_\eta(L, d_b) = \frac{[\eta](\text{star})}{[\eta](\text{linear})} \tag{32}$$

with the values of [η] so obtained for the star and linear chains having the same L and d_b.

Figure 6 shows plots of g_η against the logarithm of L. The unfilled circles represent the theoretical values of g_η, various directions of pips indicating different values of d_b indicated, and the dashed curves connect smoothly the theoretical values at constant d_b. The solid curves represent the values calculated from an interpolation formula, which are obtained and discussed in a later subsection. The horizontal line segment indicates the value 0.90 obtained by Irurzun[19] for the Gaussian regular three-arm star chain without excluded volume in the KR approximation. As L is decreased, g_η first decreases and then increases after passing through a minimum, in the range of d_b investigated. It should be noted that the behavior of g_η remarkably depends on d_b.

In the following subsections, we examine the behavior of g_η in the random-coil and rod limits and then propose an interpolation formula for g_η.

Random-Coil Limit

The value of g_η becomes a constant independent of d_b in the random-coil limit, *i.e.*, the limit of L (in units of λ^{-1}) $\to \infty$. Figure 7 shows plots of $g_\eta(L, d_b)$ against $L^{-1/2}$ for $d_b = 0.1$, 0.2, 0.3, and 0.4. All the symbols have the same meaning as those in Figure 6. The dashed curves connect smoothly the theoretical values at constant d_b and the solid straight lines indicate the respective initial tangents. It is seen that as $L^{-1/2}$ is decreased to 0 ($L \to \infty$), g_η approaches the above-mentioned value[19] 0.90 irrespective of the value of d_b. On the basis of such numerical results, it may be concluded that

$$\lim_{L \to \infty} g_\eta(L, d_b) = 0.90_0 \quad (\text{random coil}) \tag{33}$$

We note that the values of g_η for smaller d_b have been omitted in Figure 7, since we cannot make $L^{-1/2}$ ($= [(n+1)d_b]^{-1/2}$) small enough to evaluate g_η at $L^{-1/2} = 0$. We also note that the g_η value so obtained in the random-coil limit is somewhat smaller than the value 0.90_7 obtained by Zimm and Kilb[20] for the (dynamic) Gaussian spring–bead model[21,22] without excluded volume and with the preaveraged Oseen tensor.

The coil-limiting value in the KR approximation requires some comments. Khasat *et al.*[23] obtained the g_η value 0.87 for regular three-arm star polystyrene in cyclohexane at 34.5 °C (Θ), which is somewhat smaller than Irurzun's value 0.90. Further, the g_η values 0.75 and 0.63 obtained for regular four- and six-arm star polystyrenes, respectively, in cyclohexane at 34.5 °C (Θ)[24,25] are *ca.* 10% smaller than the respective theoretical values 0.82 and 0.70 obtained by Irurzun[19] for the Gaussian regular four- and six-arm star chains in the KR approximation. The KR approximation therefore seems to overestimate g_η because of the preaveraging of the Oseen tensor. It is interesting to refer the previous MC result[1] that the g_η values for the regular three-arm star freely rotating chain of bond angle 109° without the preaveraging approximation are *ca.* 5% smaller than the corresponding KR one.

Rod Limit

In the rod limit, *i.e.*, the limit of $L \to 0$, [η] in the limit of $L/d_b \to \infty$ (thin rod limit) may be written in the form (see APPENDIX C),

$$\lim_{\substack{L\to 0\\ L/d_b\to\infty}} [\eta] = \frac{\pi N_A L^3}{54M \ln(L/d_b)} \quad \text{(thin rod limit, star)} \tag{34}$$

As for the linear chain, we have

$$\lim_{\substack{L\to 0\\ L/d_b\to\infty}} [\eta] = \frac{\pi N_A L^3}{24M \ln(L/d_b)} \quad \text{(thin rod limit, linear)} \tag{35}$$

which has been obtained from the result[17] for the cylinder model of diameter d along with the relation[8] $d = 0.74 d_b$.

In the rod limit, g_η should be a function only of L/d_b, *i.e.*,

$$\lim_{L\to 0} g_\eta(L, d_b) = g_\eta^0(L/d_b) \quad \text{(rod limit)} \tag{36}$$

From eq 32 with eqs 34, 35, and 36, we have

$$\lim_{L/d_b\to\infty} g_\eta^0(L/d_b) = \frac{4}{9} \quad \text{(thin rod limit)} \tag{37}$$

It is interesting to note that the ratio g_S of the mean-square radius of gyration of the KP regular three-arm star chain to that of the linear one,[18] both having the same L, also becomes 4/9 in the rod limit.

We have also evaluated $g_\eta^0(L/d_b)$ numerically in the same manner as in the evaluation of $g_\eta(L, d_b)$ mentioned above using the expressions for $\langle R_{ij}{}^{-1}\rangle$ given by eq 21 and $\langle \mathbf{S}_i \cdot \mathbf{S}_j\rangle$ given by eqs 9 and 13 in place of those for the KP chain. Figure 8 shows plots of g_η^0 against $[\ln(L/d_b)]^{-1}$. The unfilled circles represent the values so obtained and the horizontal line segment indicates the asymptotic value 4/9 in the limit of $[\ln(L/d_b)]^{-1} \to 0$ ($L/d_b \to \infty$). As $[\ln(L/d_b)]^{-1}$ is decreased (L/d_b is increased), g_η^0 monotonically decreases to 4/9. For later convenience, we have constructed an interpolation formula for $g_\eta^0(L/d_b)$ in the range of $L/d_b \gtrsim 10$, which is given by

$$g_\eta^0(x) = \frac{4}{9}\,\frac{1 - 2.551(\ln x)^{-1} + 2.946(\ln x)^{-2}}{1 - 2.913(\ln x)^{-1} + 2.965(\ln x)^{-2}} \quad \text{for } x \gtrsim 10 \tag{38}$$

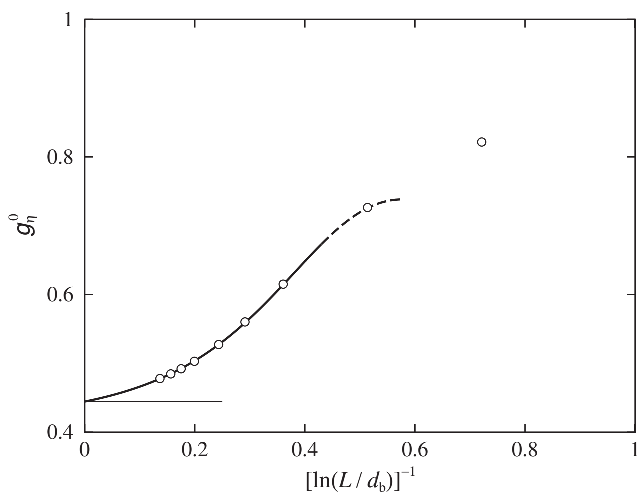

Figure 8. Plots of $g_\eta^0(L/d_b)$ against $[\ln(L/d_b)]^{-1}$. The unfilled circles represent the theoretical values. The horizontal line segment indicates the asymptotic value 4/9 in the limit of $[\ln(L/d_b)]^{-1} \to 0$ ($L/d_b \to \infty$). The curve represents the values of interpolation formula, the solid part indicating the range of $L/d_b \gtrsim 10$ (see the text).

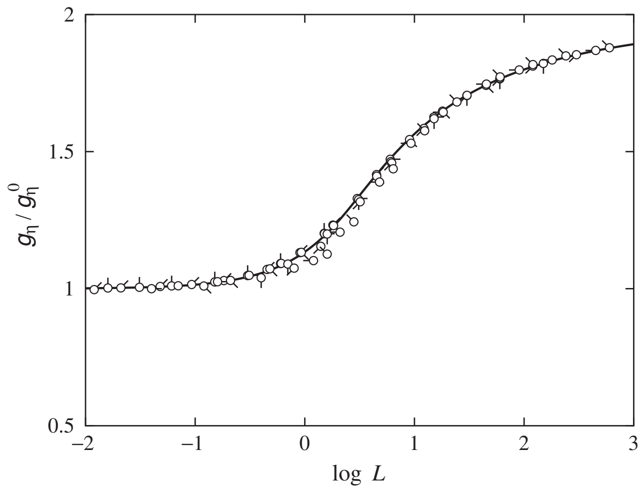

Figure 9. Plots of $g_\eta(L, d_b)/g_\eta^0(L/d_b)$ against log L. All the symbols have the same meaning as those in Figure 6. The solid curve represents the values of the interpolation formula (see the text).

In Figure 8, the curve represents the values calculated from eq 38 with $x = L/d_b$. The error in the value of $g_\eta^0(L/d_b)$ in the range of $L/d_b \gtrsim 10$ (solid part) does not exceed 0.2%.

Interpolation Formula

A simple interpolation formula, if it is available, seems to be useful for practical purposes. Figure 9 shows plots of the ratio $g_\eta(L, d_b)/g_\eta^0(L/d_b)$ against the logarithm of L, where g_η/g_η^0 has been evaluated by dividing the g_η values shown in Figure 6 by the g_η^0 values calculated from eq 38 with $x = L/d_b$. All the symbols have the same meaning as those in Figure 6. It is seen that the circles form a single composite curve almost independently of d_b for $d_b \lesssim 0.2$ and the curve monotonically increases from 1 to 2.03 [$= 0.90_0/(4/9)$] with increasing L. We have therefore assumed that g_η/g_η^0 for $d_b \lesssim 0.2$ may be represented by a function $f(L)$ of L irrespective of the value of d_b, and have constructed an empirical interpolation formula for $f(L)$, which may be written in the form,

$$\begin{aligned} f(L) &= 1 + 0.1466L - 0.01233L^2 && \text{for } L \le 3 \\ &= 2.03\,\frac{1 + 0.7106(\ln L)^{-1} + 3.219(\ln L)^{-2}}{1 + 0.9402(\ln L)^{-1} + 5.713(\ln L)^{-2}} && \text{for } L > 3 \end{aligned} \tag{39}$$

The function $f(L)$ given by eq 39 satisfies the asymptotic conditions $\lim_{L\to 0} f(L) = 1$ and $\lim_{L\to\infty} f(L) = 2.03$, which hold in the limit of $L/d_b \to \infty$. In Figure 9, the solid curve represents the values calculated from eq 39. The factor $g_\eta(L, d_b)$ may then be approximately expressed as

$$g_\eta(L, d_b) = g_\eta^0(L/d_b) f(L) \tag{40}$$

where $g_\eta^0(L/d_b)$ and $f(L)$ are given by eqs 38 and 39, respectively.

In Figure 6, the solid curves represent the approximate values calculated from eq 40 with eqs 38 and 39. It is seen that the interpolation formula for $g_\eta(L, d_b)$ so proposed may well reproduce the numerical theoretical values in the ranges of $d_b \lesssim 0.2$ and $L/d_b \gtrsim 10$. The error in the value of g_η in those ranges of d_b and L/d_b does not exceed 2%.

CONCLUSION

We have evaluated the ratio g_η of [η] of the KP regular three-arm star touched-bead model to that of the KP linear one, both having the same (reduced) total contour length L and (reduced) bead diameter d_b, in the KR approximation, and then examined its behavior as a function of L and d_b. It is found that the ratio g_η/g_η^0 of g_η to the rod-limiting value g_η^0 of g_η monotonically increases from 1 to 2.03 with increasing L and is almost independent of d_b for $d_b \lesssim 0.2$, although the behavior of g_η itself as a function of L remarkably depends on d_b. Thus we have constructed the empirical interpolation formula for $f(L) = g_\eta/g_\eta^0$ as a function of L. By the use of the expression for $f(L)$ along with that for g_η^0, which has also been constructed, the value of g_η may then be easily calculated for given L and d_b in the ranges of $d_b \lesssim 0.2$ and $L/d_b \gtrsim 10$.

APPENDIX A: AVERAGE $\langle \mathbf{S}(t^{(i)}) \cdot \mathbf{S}(t'^{(j)}) \rangle$

In this appendix, we consider the equilibrium configurational average $\langle \mathbf{S}(t^{(i)}) \cdot \mathbf{S}(t'^{(j)}) \rangle$ with $\mathbf{S}(t^{(i)})$ the vector distance from the center of mass of the KP regular f-arm star chain to the contour point on the ith arm ($i = 1, 2, \ldots, f$) with the contour distance $t^{(i)}$ from the branch point. Let L_a be the contour length of the arms and θ_{ij} the angle between the unit vectors tangent to the ith and jth arms at the branch point, so that the total contour length L of the chain becomes fL_a and $0 \leq t^{(i)}, t'^{(j)} \leq L_a$.

The average may be written in the form,

$$\begin{aligned}\langle \mathbf{S}(t^{(i)}) \cdot \mathbf{S}(t'^{(j)}) \rangle &= \frac{1}{2L} \sum_{k=1}^{f} \int_0^{L_a} [\langle R^2(t^{(i)}, s^{(k)}) \rangle + \langle R^2(t'^{(j)}, s^{(k)}) \rangle] ds^{(k)} \\ &\quad - \frac{1}{2} \langle R^2(t^{(i)}, t'^{(j)}) \rangle - \langle S^2 \rangle \end{aligned} \tag{A·1}$$

where $\langle R^2(t^{(i)}, t'^{(j)}) \rangle$ is the mean-square distance between the two contour points $t^{(i)}$ and $t'^{(j)}$ and is given by

$$\begin{aligned}\langle R^2(t^{(i)}, t'^{(j)}) \rangle &= \langle R^2(t^{(i)}, t'^{(j)}, \theta_{ij}) \rangle \quad &\text{for } i \neq j \\ &= |t^{(i)} - t'^{(j)}| - \frac{1}{2}(1 - e^{-2|t^{(i)} - t'^{(j)}|}) \quad &\text{for } i = j \end{aligned} \tag{A·2}$$

with $\langle R^2(t^{(i)}, t'^{(j)}, \theta_{ij}) \rangle$ being given by eq 19. In eq A·1, $\langle S^2 \rangle$ is the mean-square radius of gyration of the KP regular f-arm star chain and is given by[18]

$$\begin{aligned}\langle S^2 \rangle &= \frac{3f - 2}{6f^2} L - \frac{2f - 1}{4f} + \frac{1}{4L} + \left(\frac{f - 1}{4L} - \frac{f}{8L^2} \right)(1 - e^{-2L/f}) \\ &\quad - \frac{1}{2f^2} \left[1 - \left(\frac{f}{L} - \frac{f^2}{2L^2} \right)(1 - e^{-2L/f}) - \frac{f^2}{4L^2}(1 - e^{-4L/f}) \right] \sum_{i=1}^{f-1} \sum_{j=i+1}^{f} \cos\theta_{ij} \end{aligned} \tag{A·3}$$

Carrying out the integration over $s^{(k)}$, we obtain for the sum in eq A·1

$$\begin{aligned}\sum_{k=1}^{f} \int_0^{L_a} [\langle R^2(t^{(i)}, s^{(k)}) \rangle + \langle R^2(t'^{(j)}, s^{(k)}) \rangle] ds^{(k)} &= f{L_a}^2 - (2f - 1)L_a + \frac{1}{2}(f + 1) \\ &\quad + (t^{(i)})^2 + (t'^{(j)})^2 + (f - 2)L_a(t^{(i)} + t'^{(j)}) + \frac{1}{2}(f - 1)L_a(e^{-2t^{(i)}} + e^{-2t'^{(j)}}) \\ &\quad - \frac{1}{2}(f - 1)e^{-2L_a} - \frac{1}{4}(e^{-2t^{(i)}} + e^{-2t'^{(j)}}) - \frac{1}{4}e^{-2L_a}(e^{2t^{(i)}} + e^{2t'^{(j)}}) \\ &\quad - \frac{1}{2}\left[L_a - \frac{1}{2}(1 - e^{-2L_a}) \right] \left[(1 - e^{-2t^{(i)}}) \sum_{\substack{k=1 \\ \neq i}}^{f} \cos\theta_{ik} + (1 - e^{-2t'^{(j)}}) \sum_{\substack{k=1 \\ \neq j}}^{f} \cos\theta_{jk} \right] \end{aligned} \tag{A·4}$$

Equation A·1 with eqs A·2–A·4 and also with eq 19 gives $\langle \mathbf{S}(t^{(i)}) \cdot \mathbf{S}(t'^{(j)}) \rangle$. For the special case of $f = 3$ and $\theta_{ij} = 120°$ for all i and j, it reduces to eq 7 with $t^{(i)}$ and $t'^{(j)}$ in place of $t_k^{(i)}$ and $t_l^{(j)}$, respectively.

APPENDIX B: ASYMPTOTIC FORMS FOR THE MEAN RECIPROCAL OF THE END-TO-END DISTANCE OF THE ONCE-BROKEN KP CHAIN

In this appendix, we derive asymptotic forms for the mean reciprocal $\langle R^{-1}(t_1, t_2, \theta) \rangle$ of the end-to-end distance R of the once-broken KP chain of total contour length $t_1 + t_2$ such that two KP subchains 1 and 2 of contour lengths t_1 and t_2, respectively, are connected with a bending angle θ (see Figure 2).

Considering the characteristic function $I(k; t_1, t_2, \theta)$, *i.e.*, the Fourier transform of the distribution function $P(R; t_1, t_2, \theta)$ of R, defined by

$$I(k; t_1, t_2, \theta) = \int P(R; t_1, t_2, \theta) e^{i\mathbf{k}\cdot\mathbf{R}} d\mathbf{R} \tag{B·1}$$

and then integrating both sides of eq B·1 over $\mathbf{k}$, we obtain the following expression for $\langle R^{-1}(t_1, t_2, \theta) \rangle$,

$$\langle R^{-1}(t_1, t_2, \theta)\rangle = \frac{2}{\pi}\int_0^\infty I(k; t_1, t_2, \theta)dk \tag{B·2}$$

Then the problem is to obtain asymptotic forms for $I(k; t_1, t_2, \theta)$.

The distribution function $P(R; t_1, t_2, \theta)$ may be written in the form,

$$P(R; t_1, t_2, \theta) = \frac{1}{8\pi^2}\int'\left[\int G(\mathbf{R}_1|\mathbf{u}_1; t_1)G(\mathbf{R}_2|\mathbf{u}_2; t_2) \times \delta(\mathbf{R} - \mathbf{R}_1 + \mathbf{R}_2)d\mathbf{R}_1 d\mathbf{R}_2\right]d\mathbf{u}_1 d\mathbf{u}_2 \tag{B·3}$$

where $G(\mathbf{R}_p|\mathbf{u}_p; t_p)$ $(p = 1, 2)$ is the conditional distribution function (or the Green's function) of the vector distance $\mathbf{R}_p$ from the broken point to the terminal end of the pth subchain of contour length t_p with the unit vector $\mathbf{u}_p$ tangent to the pth contour at the broken point (see Figure 2) being fixed,[7] and $\delta(\mathbf{R})$ is the three-dimensional Dirac delta function. In eq B·3, $\int' \cdots d\mathbf{u}_1 d\mathbf{u}_2$ means the integrations over $\mathbf{u}_1$ and $\mathbf{u}_2$ with θ being fixed. From eq B·1 with eq B·3, we have for $I(k; t_1, t_2, \theta)$,

$$I(k; t_1, t_2, \theta) = \frac{1}{8\pi^2}\int' I^*(\mathbf{k}|\mathbf{u}_1; t_1)I(\mathbf{k}|\mathbf{u}_2; t_2)d\mathbf{u}_1 d\mathbf{u}_2 \tag{B·4}$$

where $I(\mathbf{k}|\mathbf{u}_p; t_p)$ is the characteristic function of $G(\mathbf{R}_p|\mathbf{u}_p; t_p)$ and the asterisk indicates the complex conjugate.

The characteristic function $I(\mathbf{k}|\mathbf{u}_p; t_p)$ may be expanded in terms of the (normalized) spherical harmonics Y_l^m as follows,

$$I(\mathbf{k}|\mathbf{u}_p; t_p) = (4\pi)^{1/2}\sum_{l=0}^{\infty}\mathcal{I}_l(k; t_p)\sum_{m=-l}^{l} Y_l^{m*}(\theta_p, \phi_p)Y_l^m(\chi, \omega) \tag{B·5}$$

where $\mathcal{I}_l(k; t_p)$ is the expansion coefficient and $\mathbf{u}_p = (1, \theta_p, \phi_p)$ and $\mathbf{k} = (k, \chi, \omega)$ in spherical polar coordinates in an external Cartesian coordinate system. We note that the above expression for $I(\mathbf{k}|\mathbf{u}; t)$ is essentially identical with eq 5 of ref 15 and the coefficient $\mathcal{I}_l(k; t)$ in eq B·5 is identical with $\mathcal{I}_{0ll}^{00,00}(k; t)$ in eq 5 of ref 15, although the direction of $\mathbf{u}_p$ was chosen to coincide with the z-axis of the external system in ref 15. In order to perform the integrations on the right-hand side of eq B·4 over $\mathbf{u}_1$ and $\mathbf{u}_2$ with θ being fixed, we introduce a Cartesian coordinate system associated with $\mathbf{u}_1$ and $\mathbf{u}_2$ such that $\mathbf{u}_p$ becomes equal to $(1, \tilde{\theta}_p, 0)$ in spherical polar coordinates in it with $\tilde{\theta}_1 = 0$ and $\tilde{\theta}_2 = \theta$. Let $\Omega = (\theta', \phi', \psi')$ be the Euler angles defining the orientation of the Cartesian coordinate system with respect to the external one. Then the integration $\int' \cdots d\mathbf{u}_1 d\mathbf{u}_2$ may be replaced by $\int \cdots d\Omega$ $(d\Omega = \sin\theta' d\theta' d\phi' d\psi')$ and $Y_l^m(\theta_p, \phi_p)$ may be written in terms of Ω as

$$Y_l^m(\theta_p, \phi_p) = (-1)^{(m+|m|)/2}\left(\frac{8\pi^2}{2l+1}\right)^{1/2} \times \sum_{j=-l}^{l}(-1)^{(j+|j|)/2}\mathcal{D}_l^{mj}(\Omega)Y_l^j(\tilde{\theta}_p, 0) \tag{B·6}$$

where $\mathcal{D}_l^{mj}(\Omega)$ is the (normalized) Wigner function of Ω.[26] Substituting eq B·5 with eq B·6 into eq B·4 and performing the integration over Ω, we obtain

$$I(k; t_1, t_2, \theta) = (4\pi)^{-1}\sum_{l=0}^{\infty}(2l+1)\mathcal{I}_l^*(k; t_1)\mathcal{I}_l(k; t_2)P_l(\cos\theta) \tag{B·7}$$

where we have used the relations,

$$\int \mathcal{D}_l^{mj*}(\Omega)\mathcal{D}_{l'}^{m'j'}(\Omega)d\Omega = \delta_{ll'}\delta_{mm'}\delta_{jj'} \tag{B·8}$$

$$\sum_{m=-l}^{l} Y_l^{m*}(\chi, \omega)\, Y_l^m(\chi, \omega) = \frac{2l+1}{4\pi} \tag{B·9}$$

$$Y_l^m(0, 0) = \delta_{m0}\left(\frac{2l+1}{4\pi}\right)^{1/2} \tag{B·10}$$

$$Y_l^0(\theta, 0) = \left(\frac{2l+1}{4\pi}\right)^{1/2} P_l(\cos\theta) \tag{B·11}$$

and $P_l(x)$ is the Legendre polynomial.

The asymptotic form for $\mathcal{I}_l(k; t_p)$ in the case of $t_p \gg 1$ may be obtained in the Daniels approximation,[7,12–14] and its general expression [for the helical wormlike (HW) chain[7]] is given by eq 44 of ref 14 with $l_1 = 0$, $l_2 = l_3 = l$, $m_1 = m_2 = 0$, and $j_1 = j_2 = 0$. On retaining terms up to $\mathcal{O}(t_p^{-2})$ (*i.e.*, the second Daniels approximation), the necessary $\mathcal{I}_l(k; t_p)$'s with $l = 0, 1, \ldots, 4$ can be straightforwardly evaluated to be

$$\mathcal{I}_l(k; t_p) = (4\pi)^{1/2}(2l+1)^{-1}e^{-t_p k^2/6}(ik)^l g_l(k; t_p) \tag{B·12}$$

with i the imaginary unit and

$$\begin{aligned}
g_0(k; t_p) &= 1 + \frac{1}{12}k^2 + \left(\frac{107}{6480} - \frac{11}{1080}t_p\right)k^4 - \frac{607}{272160}t_p k^6 + \frac{121}{2332800}t_p^{\,2}k^8 \\
g_1(k; t_p) &= \frac{1}{2} + \frac{13}{180}k^2 - \frac{11}{2160}t_p k^4 \\
g_2(k; t_p) &= \frac{1}{18} + \frac{85}{9072}k^2 - \frac{11}{19440}t_p k^4 \\
g_3(k; t_p) &= \frac{1}{360} \\
g_4(k; t_p) &= \frac{1}{12600}
\end{aligned} \tag{B·13}$$

The asymptotic form for $\mathcal{I}_l(k; t_p)$ in the case of $t_p \ll 1$, on the other hand, may be obtained by the ϵ method,[7,15,16] and its general expression (for the HW chain) is given by eq 10 of ref 16. On retaining terms up to $\mathcal{O}(t_p^{\,2})$, the necessary $\mathcal{I}_l(k; t_p)$'s with $l = 0, 1, \ldots, 4$ may be explicitly written in the form,

$$\mathcal{I}_l(k; t_p) = (4\pi)^{1/2}i^l\left[(1 + \langle\delta_l\rangle)j_l(kt_p) - \frac{1}{2}kt_p(\langle\epsilon\rangle + \langle\delta_l\epsilon\rangle)j_{l+1}(kt_p) + \frac{1}{8}(kt_p)^2\langle\epsilon^2\rangle\, j_{l+2}(kt_p)\right] \tag{B·14}$$

where $j_l(x)$ is the spherical Bessel function of the first kind and ϵ and δ_l are relative deviations of the square end-to-end distance ${R_p}^2$ and of the quantity ${R_p}^l Y_l^0(\theta_p, \phi_p) Y_l^0(\Theta_p, \Phi_p)$ with $\mathbf{R}_p = (R_p, \Theta_p, \Phi_p)$ in spherical polar coordinates in the external system, respectively, of the KP subchain p, from the respective rod-limiting values. We note that δ_l is identical with $\delta_{0ll}^{00,00}$ defined for the HW chain by eq 4 of ref 16. The equilibrium averages $\langle\epsilon\rangle$, $\langle\epsilon^2\rangle$, $\langle\delta_l\rangle$, and $\langle\delta_l\epsilon\rangle$ in eq B·14 are given by eqs 5, 6, and 7 of ref 16 and are explicitly given by

$$\langle\epsilon\rangle = -\frac{2}{3}t_p + \frac{1}{3}{t_p}^2$$

$$\langle\epsilon^2\rangle = \frac{28}{45}{t_p}^2$$

$$\langle\delta_l\rangle = 4\pi\langle {R_p}^l Y_l^0(\theta_p, \phi_p) Y_l^0(\Theta_p, \Phi_p)\rangle {t_p}^{-l} - 1$$

$$\langle\delta_l\epsilon\rangle = 4\pi\langle {R_p}^{l+2} Y_l^0(\theta_p, \phi_p) Y_l^0(\Theta_p, \Phi_p)\rangle {t_p}^{-l-2} - (1 + \langle\epsilon\rangle + \langle\delta_l\rangle) \tag{B·15}$$

The moments $\langle {R_p}^l Y_l^0 Y_l^0\rangle$ and $\langle R_p^{l+2} Y_l^0 Y_l^0\rangle$ in eqs B·15 may be evaluated analytically by the use of the operational method.[7,27] Although the details of rather lengthy calculations are omitted here, we can finally obtain

$$\mathcal{I}_0(k;t_p) = (4\pi)^{1/2}\left[j_0(kt_p) - \frac{1}{6}{t_p}^2(t_p - 2)kj_1(kt_p) + \frac{7}{90}{t_p}^4k^2j_2(kt_p)\right]$$

$$\mathcal{I}_1(k;t_p) = (4\pi)^{1/2}i\left[\left(\frac{2}{3}{t_p}^2 - t_p + 1\right)j_1(kt_p) - \frac{1}{30}{t_p}^2(19t_p - 10)kj_2(kt_p) + \frac{7}{90}{t_p}^4k^2j_3(kt_p)\right]$$

$$\mathcal{I}_2(k;t_p) = (4\pi)^{1/2}\left[-\left(\frac{13}{3}{t_p}^2 - \frac{8}{3}t_p + 1\right)j_2(kt_p) + \frac{1}{90}{t_p}^2(127t_p - 30)kj_3(kt_p) - \frac{7}{90}{t_p}^4k^2j_4(kt_p)\right]$$

$$\mathcal{I}_3(k;t_p) = (4\pi)^{1/2}i\left[-\left(\frac{73}{5}{t_p}^2 - 5t_p + 1\right)j_3(kt_p) + \frac{1}{6}{t_p}^2(15t_p - 2)kj_4(kt_p) - \frac{7}{90}{t_p}^4k^2j_5(kt_p)\right]$$

$$\mathcal{I}_4(k;t_p) = (4\pi)^{1/2}\left[\left(\frac{221}{5}{t_p}^2 - 8t_p + 1\right)j_4(kt_p) - \frac{1}{30}{t_p}^2(117t_p - 10)kj_5(kt_p) + \frac{7}{90}{t_p}^4k^2j_6(kt_p)\right] \tag{B·16}$$

Substituting eq B·7 with $\mathcal{I}_l(k;t_1)$ and $\mathcal{I}_l(k;t_2)$, both given by eq B·12 with eq B·13, into eq B·2 and performing the integration over k, we have for the asymptotic form for $\langle R^{-1}(t_1, t_2, \theta)\rangle$ in the case of $t_1 \gg 1$ and $t_2 \gg 1$

$$\langle R^{-1}(t_1, t_2, \theta)\rangle = \left[\frac{6}{\pi(t_1 + t_2)}\right]^{1/2}\left\{1 - \frac{1}{40(t_1 + t_2)} - \frac{73}{4480(t_1 + t_2)^2} + \left[\frac{1}{4(t_1 + t_2)} + \frac{49}{160(t_1 + t_2)^2}\right](1 + \cos\theta) - \frac{1}{40(t_1 + t_2)^2}(1 - \cos^2\theta)\right\} \quad (t_1 \gg 1,\ t_2 \gg 1) \tag{B·17}$$

If we use $\mathcal{I}_l(k;t_2)$ given by eq B·16 in the above calculation, we have the asymptotic form in the case of $t_1 \gg 1$ and $t_2 \ll 1$

$$\langle R^{-1}(t_1, t_2, \theta)\rangle = \left(\frac{6}{\pi t_1}\right)^{1/2}\left[1 - \frac{1}{40t_1} - \frac{t_2}{2t_1} - \frac{73}{4480{t_1}^2} + \frac{3t_2}{80{t_1}^2} + \frac{3{t_2}^2}{8{t_1}^2} + \left(\frac{1}{2t_1} - \frac{3}{80t_1^2}\right)(t_2 - {t_2}^2)(1 + \cos\theta) - \frac{3{t_2}^2}{20{t_1}^2}(1 - \cos^2\theta)\right] \quad (t_1 \gg 1,\ t_2 \ll 1) \tag{B·18}$$

Considering the fact that $\langle R^2(t_1, t_2, \theta)\rangle$ given by eq 19 may be expanded in the above two cases as follows,

$$\begin{aligned}\langle R^2(t_1, t_2, \theta)\rangle &= t_1 + t_2 - \frac{1}{2} - \frac{1}{2}(1 + \cos\theta) && (t_1 \gg 1,\ t_2 \gg 1)\\ &= t_1 + t_2 - \frac{1}{2} - (t_2 - {t_2}^2)(1 + \cos\theta) && (t_1 \gg 1,\ t_2 \ll 1)\end{aligned} \tag{B·19}$$

the expressions for $\langle R^2(t_1, t_2, \theta)\rangle$ in the two cases given by eqs B·17 and B·18 may be rewritten as those given by eqs 16 and 17, respectively.

As for the asymptotic form in the case of $t_1 \ll 1$ and $t_2 \ll 1$, we have applied the ϵ method directly to $\langle R^{-1}(t_1, t_2, \theta)\rangle$ and derived the expression given by eq 18, which is valid up to $\mathcal{O}({t_1}^2)$, $\mathcal{O}({t_2}^2)$, and $\mathcal{O}(t_1t_2)$. We note that in the derivation ϵ has been chosen to be the relative deviation of R^2 from $\langle R^2\rangle$ given by eq 19.

APPENDIX C: ASYMPTOTIC FORM FOR THE INTRINSIC VISCOSITY OF THE REGULAR THREE-ARM STAR IN THE ROD LIMIT

In this appendix, we derive the asymptotic solution in the limit of $L/d_\mathrm{b} \to \infty$ (thin or long rod limit) for [η] of the KP regular three-arm star in the rod limit. In the thin rod limit, $[\eta]_\mathrm{E}$

may be ignored, so that we only consider $[\eta]_{\rm KR}$ given by eq 2. Further, the distance between the adjacent beads, *i.e.*, $d_{\rm b}$ for the touched-bead model, becomes very small compared to L, so that we may convert the sums in eqs 2 and 4 to integrals. Eq 2 with eq 4 may then be rewritten in the form,

$$[\eta] = \frac{3N_{\rm A}L}{M}\int_0^1 \psi_0(x,x)dx \tag{C·1}$$

where $\psi_0(x,y)$ is the solution of the set of integral equations,

$$\int_0^1 [K_0(x,\xi)\psi_0(\xi,y) + 2K_1(x,\xi)\psi_1(\xi,y)]d\xi = g_0(x,y)$$

$$\int_0^1 [K_0(x,\xi)\psi_1(\xi,y) + K_1(x,\xi)\psi_0(\xi,y) + K_1(x,\xi)\psi_1(\xi,y)]d\xi = g_1(x,y) \tag{C·2}$$

In eq C·2, $K_0(x,y)$ and $K_1(x,y)$ are the continuous versions of the mean reciprocal of the distance between the centers of two beads on the same arm and on different ones, respectively, and $g_0(x,y)$ and $g_1(x,y)$ are those of $\pi\langle \mathbf{S}_i\cdot\mathbf{S}_j\rangle$ for the centers of two beads on the same arm and on different ones, respectively. They are explicitly given by

$$\begin{aligned} K_0(x,y) &= \frac{3}{L}|x-y|^{-1} \quad &&\text{for } |x-y| \geq 3d_{\rm b}/L \\ &= 0 &&\text{for } |x-y| < 3d_{\rm b}/L \end{aligned} \tag{C·3}$$

$$K_1(x,y) = \frac{3}{L}(x^2+y^2+xy)^{-1/2} \tag{C·4}$$

$$g_0(x,y) = \frac{\pi L}{9}xy \tag{C·5}$$

$$g_1(x,y) = -\frac{\pi L}{18}xy \tag{C·6}$$

Now we expand $\psi_0(x,y)$, $\psi_1(x,y)$, $g_0(x,y)$, and $g_1(x,y)$ in terms of the shifted Legendre polynomial $\tilde{P}_l(x)$ as, for example,

$$\psi_0(x,y) = \sum_{i=0}^{\infty}\sum_{j=0}^{\infty}\psi_{0,ij}\tilde{P}_i(x)\tilde{P}_j(y) \tag{C·7}$$

where $\tilde{P}_l(x)$ $(l = 0,1,2,\ldots)$ is defined by

$$\tilde{P}_l(x) = (-1)^l P_l(2x-1) \tag{C·8}$$

We note that $\tilde{P}_l(x)$ satisfies the following orthogonality relation,

$$\int_0^1 \tilde{P}_l(x)\tilde{P}_{l'}(x)dx = \frac{\delta_{ll'}}{2l+1} \tag{C·9}$$

Then eq C·1 may be written in terms of the expansion coefficients $\psi_{0,ij}$ as

$$[\eta] = \frac{3N_{\rm A}L}{M}\sum_{i=0}^{\infty}\frac{\psi_{0,ii}}{2i+1} \tag{C·10}$$

and the integral equations C·2 may be converted to a set of linear simultaneous equations, which may be written in the following matrix form,

$$\mathbf{K}\cdot\boldsymbol{\psi} = \mathbf{g} \tag{C·11}$$

The three matrices $\mathbf{K}$, $\boldsymbol{\psi}$, and $\mathbf{g}$ in eq C·11 have the same structure composed of 9 submatrices and may be explicitly written as, for example,

$$\mathbf{K} = \begin{pmatrix} \mathbf{K}_0 & \mathbf{K}_1 & \mathbf{K}_1 \\ \mathbf{K}_1 & \mathbf{K}_0 & \mathbf{K}_1 \\ \mathbf{K}_1 & \mathbf{K}_1 & \mathbf{K}_0 \end{pmatrix} \tag{C·12}$$

where $\mathbf{K}_0$ and $\mathbf{K}_1$ are the symmetric matrices whose ij elements are given by

$$K_{k,ij} = \int_0^1\int_0^1 K_k(x,y)\tilde{P}_i(x)\tilde{P}_j(y)dxdy \quad (k=0,1) \tag{C·13}$$

Similarly, $\boldsymbol{\psi}$ ($\mathbf{g}$) is composed of $\boldsymbol{\psi}_0$ and $\boldsymbol{\psi}_1$ ($\mathbf{g}_0$ and $\mathbf{g}_1$) whose ij elements are the expansion coefficients $\psi_{0,ij}$ and $\psi_{1,ij}$ ($g_{0,ij}$ and $g_{1,ij}$), respectively.

It can be shown in the limit of $L/d_{\rm b} \to \infty$ that the diagonal elements $K_{0,ii}$ of $\mathbf{K}$ are proportional to $L^{-1}\ln(L/d_{\rm b})$ while the off-diagonal ones $K_{0,ij}$ $(i \neq j)$ and $K_{1,ij}$ are of $\mathcal{O}(L^{-1}[\ln(L/d_{\rm b})]^0)$ at most. Further the elements $g_{0,ij}$ and $g_{1,ij}$ of $\mathbf{g}_0$ and $\mathbf{g}_1$, respectively, may be calculated to be

$$g_{0,ij} = \frac{1}{36}\pi L(2i+1)(2j+1)\left(\delta_{i0}-\frac{1}{3}\delta_{i1}\right)\left(\delta_{j0}-\frac{1}{3}\delta_{j1}\right) \tag{C·14}$$

$$g_{1,ij} = -\frac{1}{72}\pi L(2i+1)(2j+1)\left(\delta_{i0}-\frac{1}{3}\delta_{i1}\right)\left(\delta_{j0}-\frac{1}{3}\delta_{j1}\right) \tag{C·15}$$

Then we have

$$\psi_{ii} = \frac{\pi L}{36(2i+1)}[\delta_{i0}K_{0,00}^{-1} + \delta_{i1}K_{0,11}^{-1} + \mathcal{O}(L[\ln(L/d_{\rm b})]^{-2})] \tag{C·16}$$

and $[\eta]$ may be written in the form

$$\lim_{L/d_{\rm b}\to\infty}[\eta] = \frac{\pi N_{\rm A}L^2}{12M}\left(K_{0,00}^{-1} + \frac{1}{9}K_{0,11}^{-1}\right) \tag{C·17}$$

The necessary elements $K_{0,00}$ and $K_{0,11}$ of $\mathbf{K}$ are calculated to be

$$\begin{aligned} K_{0,00} &= 6\ln(L/d_{\rm b})/L \\ K_{0,11} &= 2\ln(L/d_{\rm b})/L \end{aligned} \tag{C·18}$$

Substitution of eqs C·18 into eq C·17 leads to eq 34.

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