SHORT COMMUNICATION

Remark on Yamakawa—Fujii's Paper Concerning the Intrinsic Viscosity of Rod-like Macromolecules

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Recently, Yamakawa and Fujii¹ formulated an integral equation basic to the calculation of the intrinsic viscosity, $[\eta]$, of rod-like macromolecules by application of the Oseen—Burgers approximation coupled with the preaveraging of the Oseen tensor for hydrodynamic interactions. This equation was solved numerically for values of length-to-diameter ratio, L/d , equal to and larger than 100; its asymptotic solution for long rods was also derived analytically.¹ One of the features revealed by these calculations was that the approach of the numerically obtained values of $[\eta]$ to the asymptotic relation was surprisingly slow, as seen from the typical results given below:

L/d	100	1,000	10,000
$[\eta]/[\eta]_0$	1.065	1.033	1.021

where $[\eta]_0$ denotes the $[\eta]$ given by Yamakawa—Fujii's asymptotic relation. Such feature, however, is not readily compatible with our physical prediction that rods with L/d as large as 1000 should be long enough to behave hydrodynamically like infinitely long ones. Thus there has arisen in the author's mind a question of whether the numerical procedure used by Yamakawa and Fujii was really appropriate to obtain accurate solutions of the integral equation concerned. In fact, this integral equation has a kernel behaving like a delta function for large values of L/d , so that its numerical solution ought to be a task requiring great caution. The present communication purports to calculate its approximate solutions by determining terms beyond the asymptotic relation of Yamakawa and Fujii, in the hope that such analytic

solutions will serve to find an answer to the question raised above.

The formulation of Yamakawa and Fujii¹ gives for the intrinsic viscosity of a straight rod with length L and diameter d

$$[\eta] = \frac{\pi N_A L^3}{18M} A^{11}/|A| \quad (1)$$

where N_A is Avogadro's number, M is the molecular weight of the rod, $|A|$ is the determinant whose elements $(i, j=0, 1, \dots)$ are given by

$$a_{ij} = a_{ji} = \int_{-1}^1 \int_{-1}^1 \frac{P_i(t)P_j(x)dt dx}{[(x-t)^2 + (d/L)^2]^{1/2}} \quad (2)$$

with P_i being the Legendre polynomial of the i -th order, and A^{ij} is the cofactor for the element a_{ij} . If the value of $A^{11}/|A|$ for the $|A|$ approximated by an $m \times m$ determinant is denoted by $(A^{11}/|A|)_m$ and if use is made of the fact that $a_{ij}=0$ for $i+j=\text{odd integer}$, we find that

$$(A^{11}/|A|)_2 = (A^{11}/|A|)_3 = 1/a_{11} \quad (3)$$

$$(A^{11}/|A|)_4 = (A^{11}/|A|)_5 = 1/(a_{11} - a_{13}^2 a_{33}^{-1}) \quad (4)$$

$$(A^{11}/|A|)_6 = (A^{11}/|A|)_7 = 1/[a_{11} + (2a_{13}a_{35}a_{15} - a_{13}^2 a_{55} - a_{15}^2 a_{33})/B] \quad (5)$$

where

$$B = a_{33}a_{55} - a_{35}^2 \quad (6)$$

We have calculated exactly all the a_{ij} terms contained in these expressions from eq 2. The results are too lengthy to present here in full. For example, a_{11} is given by

Table I. Values of $[\eta]/[\eta]_0$

L/d	$[\eta]/[\eta]_0$			Y—F
	$2 \times 2, 3 \times 3^a$	$4 \times 4, 5 \times 5$	$6 \times 6, 7 \times 7$	
50	0.9901	1.0174	1.0269	
100	0.9959	1.0146	1.0215	1.0646
200	0.9983	1.0116	1.0165	1.0529
300	0.9990	1.0100	1.0140	
500	0.9994	1.0084	1.0115	1.0380
1000	0.9997	1.0066	1.0089	1.0327
5000	1.0000	1.0041	1.0053	1.0237
10000	1.0000	1.0034	1.0041	1.0207

^a Rank of determinant $|A|$ used for the computation of $[\eta]$.

$$a_{11} = (4/3) \{ \ln(L/d) + [(L/d)^2 + (1/4)]^{1/2} + \ln 2 - (7/6)[4 + (d/L)^2]^{1/2} + (3/2)(d/L) - (1/6)(d/L)^2[4 + (d/L)^2]^{1/2} + (1/6)(d/L)^3 \} \quad (7)$$

The asymptotic limit of $[\eta]$ for very long rods, denoted by $[\eta]_0$, is exactly given by

$$[\eta]_0 = \frac{\pi N_A L^3}{24M[\ln(L/d) + 2 \ln 2 - (7/3)]} \quad (8)$$

which confirms the result of Yamakawa and Fujii.¹

Table I shows values of $[\eta]/[\eta]_0$ computed from the present analytic results for L/d ranging from 50 to 10000. The last column of the table lists the corresponding values computed from Yamakawa—Fujii's numerical results.

Looking at the numerical values from the second through the forth column, it appears that, though rather slowly, the analytic solutions converge with the increase in the rank of the determinant $|A|$. The limits of convergence cannot be assessed with accuracy, but it is quite unlikely that they will come close to Yamakawa—Fujii's numerical results. In fact, the analytic solutions are essentially indistinguishable from the asymptotic values for L/d larger than 1000, as should be expected from physical intuition, but differing distinctly from Yamakawa—Fujii's numerical solutions.

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REFERENCE

1. H. Yamakawa and M. Fujii, *Macromolecules*, **7**, 128 (1974).