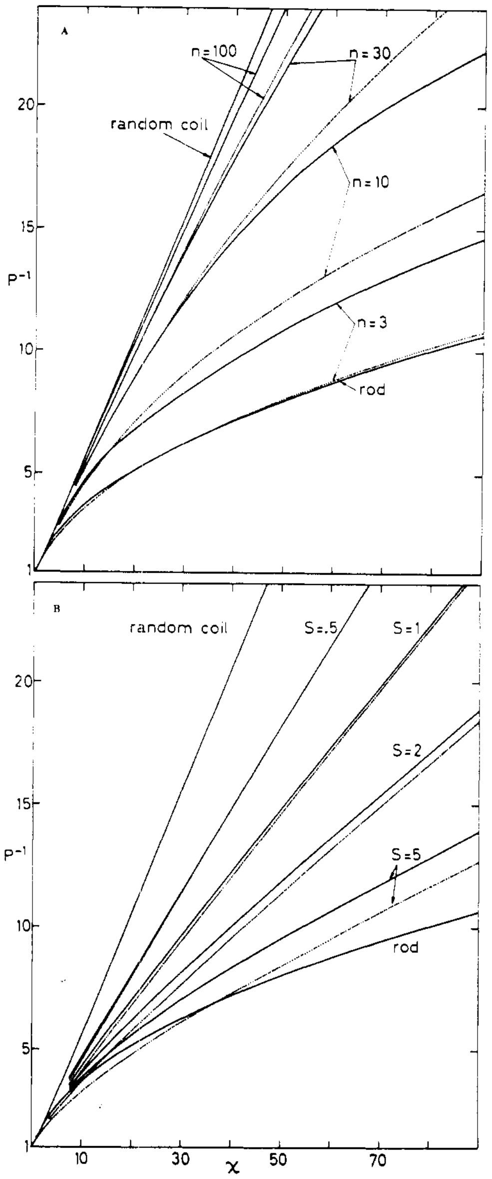

Figure 1. Reciprocal scattering factor for (A) model ZZ; (B) model CP: ———, values of the exact $1/P$; · · · · · ·, values of the gaussian approximation $1/P'$.

Although the sign of $1/P - 1/P'$ is the same for the two models here presented, the magnitude and its variation with χ is very different. Even for values of P very close to the random coil ones, the error committed with P' in the ZZ model is large. In fact, Figure 1A shows that $1/P - 1/P'$ gets easily larger than $1/P$ (random coil) $- 1/P$. In the case of model CP, the error is small except at high separations from random coil behavior. However, in the region of low χ (around $\chi \lesssim 20$), $1/P - 1/P'$ becomes important relative to $1/P$ even for $S = 1$. It should be noted that the $1/P'$ curves of both models (and also the $1/P$ curves of model CP) cross under the exact results for a rigid rod. This situation is illustrated by the approximate curves for $n = 3$ and $S = 2, 5$. For higher n, or lower S, the cross-point moves toward $\chi \rightarrow 0$ and is not shown in the figure.

The conclusion is that, although the two models considered are strong idealizations of the chain and tend to the random coil as a limit case (when $n \rightarrow N$, or $S \rightarrow 0$), the error involved in the use of the gaussian aproximation for P is appreciable even at moderate degrees of chain extension (at least, in some region of χ).

For molecular scattering ($\chi < 3$),[16] however, the error will usually be quite small, as remarked by Flory and Jernigan.[7] Nevertheless, the range of χ covered by visible light can be extended beyond this limit. Values up to $\chi \simeq 50$ have been reached by Smith and Carpenter[17] with polystyrene in benzene at 30° using 3650 Å wavelength.

Addendum. The work of Sanchez and Frankenberg[18] was, unfortunately, not available to the present author at the time of writing. Equation 49 in their paper appears to be a slight refinement of the CP model. Also, the constant value of $\langle\cos(ij)\rangle$ in their correlated chain seems to indicate a relationship with the model of Peterlin.[5]

(16) Molecular scattering as defined by P. J. Flory in "Statistical Mechanics of Chain Molecules," Interscience Publishers, New York, N. Y., 1969, p 347.

(17) T. E. Smith and D. K. Carpenter, *Macromolecules*, **1**, 204 (1968).

(18) I. C. Sanchez and C. von Frankenberg, *ibid.*, **2**, 666 (1969).

Excluded Volume in Flexible Linear Macromolecules

HIDEMATSU SUZUKI

Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611, Japan.

Received February 24, 1970

One approach to the construction of approximate theories of the excluded-volume effect is to solve the Fixman differential equation for the end-to-end distance **R** (or the radius of gyration S)[1,2]

$$\frac{\partial\langle\mathbf{R}^2\rangle}{\partial\beta} = \sum_{i>j}\int \mathbf{R}^2[P(\mathbf{R})P(\mathrm{O}_{ij}) - P(\mathbf{R},\mathrm{O}_{ij})]\,d\mathbf{R} \qquad (1)$$

under appropriate assumptions. Here $\langle\mathbf{R}^2\rangle$ denotes the mean-square end-to-end distance; β is the cluster integral; and P's represent the probabilities in the perturbed state. The flexible linear macromolecule is considered to be composed of N identical segments, each with a root-mean-square length a. As usual, the uniform expansion approximation is adopted; thus the unknown probabilities, $P(\mathbf{R})$, $P(\mathrm{O}_{ij})$, and $P(\mathbf{R}, \mathrm{O}_{ij})$ are replaced by the corresponding random-flight probabilities with a conventional length αa. Equation 1 may be then rewritten as[1]

$$\partial\alpha_{\mathrm{R}}^2/\partial z = C_1/\alpha \qquad (2)$$

with

$$\alpha_{\mathrm{R}}^2 = \langle\mathbf{R}^2\rangle/\langle\mathbf{R}^2\rangle_0 = \langle\mathbf{R}^2\rangle/Na^2 \qquad (3)$$

$$z = (3/2\pi a^2)^{3/2}\beta N^{1/2} \qquad (4)$$

and $C_1 = {}^4/_3$. Here α_{R} is called the expansion factor for the end-to-end distance; the subscript 0 refers to the unperturbed state; and eq 4 expresses the definition of the excluded-volume variable z.

(1) M. Fixman, *J. Chem. Phys.*, **23**, 1656 (1955).

(2) M. Fixman, *ibid.*, **36**, 306, 3123 (1962).

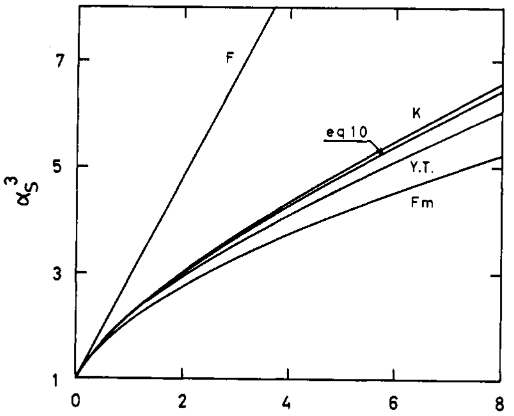

Figure 1. Comparison of the α_S^2 *vs.* z curve calculated from eq 10 with curve F (the Fixman theory, eq 12), curve K (the Koyama theory, eq 13), curve Y.T. (the Yamakawa–Tanaka theory, eq 11), and curve Fm (the modified Flory theory, eq 14).

Needless to say, α is an unknown function of z, and hence series expansion is applied in order to determine $\alpha(z)$ in an expanded form. Perturbation theories[1,3,4] have been able to give the exact coefficients for α_R^2 up to the third-order term

$$\alpha_R^2 = 1 + C_1z - C_2z^2 + C_3z^3 - \ldots \tag{5}$$

with $C_1 = {}^4/_3 = 1.333$, $C_2 = 2.075$, and $C_3 = 6.459$. Differentiating eq 5 with respect to z and substituting it into eq 2, we find the square of α as

$$\alpha^2 = 1 + k_1z + k_2z^2 + \ldots \tag{6}$$

with

$$k_1 = 4C_2/C_1 \tag{7a}$$

and

$$k_2 = 12(C_2/C_1)^2 - 6(C_3/C_1) \tag{7b}$$

These coefficients are evaluated with the numerical values of C_1, C_2, and C_3: it is found that k_1 is as large as 6.22₅, and *curiously enough, k_2 becomes zero.* The expanded forms of α, α^3, and so on, are also obtainable, but they have nonzero values for the coefficient of the z^2 term. Thus, for easy performance of integration of eq 2, an approximate expression of $\alpha^2 = 1 + k_1z + O(z^3)$ may be preferred to the others. In addition this approximation will be better than that of Ptitsyn[5] which represents α as $\alpha^3 = 1 + Kz$ with an adjustable constant K. We then obtain the following equation which satisfies the third-order perturbation theory at least

$$\alpha_R^2 = 0.572 + 0.428(1 + 6.23z)^{1/2} \tag{8}$$

This equation is just one of the Yamakawa–Tanaka equations,[4] first derived by the method of a hierarchy of differential equations.

This procedure is also applicable to the calculation of the expansion factor α_S for the radius of gyration, which is more important than the end-to-end distance from the experimental point of view. It has already been determined[1,6] that

$$\alpha_S^2 = 1 + c_1z - c_2z^2 + \ldots \tag{9}$$

with $c_1 = 1.276$ and $c_2 = 2.082$, so the final result is given as

$$\alpha_S^2 = 0.609 + 0.391(1 + 6.53z)^{1/2} \tag{10}$$

under the assumption that α is written as $\alpha^2 = 1 + (4c_2/c_1)z$. The Taylor expansion of eq 10 yields the value 6.79₃ for the coefficient of the z^3 term. Although the exact value of c_3 is not available as yet, this value 6.79₃ is quite close to the exact value 6.459 of the corresponding coefficient in eq 5. Yanakawa and Tanaka[4] assumed the latter value for the unknown coefficient c_3 and derived

$$\alpha_S^2 = 0.541 + 0.459(1 + 6.04z)^{0.46} \tag{11}$$

Their theory, if combined with the former value 6.79₃, leads to eq 10. The difference between eq 10 and 11 simply reflects the difference between the assumed values of c_3.

The present equation for α_S is illustrated in Figure 1 with eq 11 and some others displayed by the following

(Fixman)[2] $$\alpha_S^3 = 1 + 1.91z \tag{12}$$

$$\alpha_S^4 - \alpha_S^2 = 1.276zg(\alpha_S)$$

(Koyama)[7] $$g(\alpha_S) = (\alpha_S^2 + 3)/4\alpha_S \tag{13}$$

and

(Flory)[8] $$\alpha_S^5 - \alpha_S^3 = 1.276z \tag{14}$$

Interestingly this figure shows that the present work is almost indistinguishable from the Koyama theory,[7] which is based on the approximate estimation of the average intramolecular potential by means of an ellipsoid model. Apparently the uniform expansion approximation used here is rather poor for large values of z, and it is natural that the asymptotic behaviors differ from each other. The validity of eq 8 and 10 must be examined by higher order perturbation calculations.

Acknowledgments. The author cannot resist the pleasure of expressing his gratitude to Professor H. Inagaki, Professor T. Kotaka, and Professor M. Kurata of this institute for kindly giving him invaluable suggestions on preparation of the manuscript.

---

(3) E. Teramoto, *Busseiron Kenkyu*, **39**, 1 (1951); **40**, 18 (1951); **41**, 14 (1951); B. H. Zimm, W. H. Stockmayer, and M. Fixman, *J. Chem. Phys.*, **21**, 1716 (1953).

(4) H. Yamakawa and G. Tanaka, *J. Chem. Phys.*, **47**, 3991 (1967).

(5) O. B. Ptitsyn, *Vysokomol. Soedin.*, **3**, 1673 (1961).

(6) H. Yamakawa, A. Aoki, and G. Tanaka, *J. Chem. Phys.*, **45**, 1928 (1966).

(7) R. Koyama, *J. Phys. Soc. Jap.*, **22**, 973 (1967).

(8) P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949); W. H. Stockmayer, *J. Polym. Sci.*, **15**, 595 (1955).