The parameters derived from the two permeation curves (3) and (4) are listed in Table IV. The coefficients, which in Figure 5 are given in atmospheric pressure units, are converted to centimeters to facilitate comparison with the CO_2, O_2, and N_2 data. Approximate solubility and diffusion coefficients of N_2O_4 at 25° are given also. The solubility coefficient was derived from the directly measured solubilities (Table II) by extrapolation to 25°. A correction was made for the solubility of the NO_2 present in the gas phase at 25°.

A comparison of the solubility and diffusion coefficients of N_2O_4 and of CO_2, O_2, N_2 indicates a common pattern. The solubility coefficients of the gases correlate quite well with their boiling points, as has been found for other gas–polymer systems.[8] Similarly, the reduction in the N_2O_4 diffusion coefficient by a factor of about 4 compared to CO_2 appears to be reasonable in view of the much larger size of the N_2O_4 molecule. Thus, N_2O_4, like the other gases, apparently does not interact with PTFE.

In contrast, the NO_2 data do not fit the pattern at all. Although the NO_2 molecule has approximately the same size as CO_2, its activation energy of diffusion is about twice and its heat of solution about three times that of CO_2. Also, its diffusion and solubility coefficients at 25° are smaller and larger, respectively, by orders of magnitude. These observations suggest that the highly polar NO_2 molecule interacts strongly with PTFE.

A systematic analysis of the data in terms of molecular dimensions and interchain forces is not only of considerable interest, but is essential for a more detailed and quantitative understanding of diffusion mechanisms. This analysis must however be postponed until data for a larger number of permeants and PTFE samples of different degree of crystallinity are available.

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(8) G. T. van Amerongen, *Rubber Chem. Technol.*, **37**, 1065, (1964).

Notes

Validity of the Gaussian Approximation to the Polymer Scattering Factor in Simple Chain Models[1]

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The particle scattering factor P, for an isolated polymer chain in equilibrium, can be written as

$$P(\omega) = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left\langle\frac{\sin \omega r_{ij}}{\omega r_{ij}}\right\rangle \tag{1}$$

N being the total number of scattering elements in the chain, r_{ij} the distance between elements i and j, and $\omega = (2\pi/\lambda)2 \sin (\theta/2)$, where λ is wavelength and θ scattering angle.

When the segment distribution is gaussian, the average in eq 1 can be expressed in terms of the second moment $\langle r_{ij}^2\rangle$ of the distribution,[2] and P reads

$$P(\omega) = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\exp\left(-\frac{\omega^2}{6}\langle r_{ij}^2\rangle\right) \tag{2}$$

However, gaussian statistics represent only a particular behavior of the chain, and many cases of interest correspond to coils with nongaussian effects.

Since very little is known about the form of the distribution for nongaussian coils, a general procedure to calculate P for such coils is to assume that eq 2 is still valid, and to incorporate the nongaussian behavior by substituting for $\langle r_{ij}^2\rangle$ a form which adequately represents the actual mean quadratic separation between segments. This *ad hoc* procedure has been extensively used to study the influence on P of excluded volume,[3–5] chain stiffness,[5,6] and the detailed structure of the chain[7] (represented by the rotational isomeric model). It is, thus, of great interest to estimate the error that is committed by these type of calculations which apply the gaussian form (2) to nongaussian model chains. A step in this direction is the work of Nagai, who showed[8] that, for a generic distribution, $\langle \sin \omega r_{ij}/\omega r_{ij}\rangle$ can be expanded in a power series whose zeroth order term is the gaussian exponential $\exp(-\omega^2 \cdot \langle r_{ij}^2\rangle/6)$.

The purpose of this note is to determine, numerically, the error committed with the gaussian approximation (2) in the case of two very simple nongaussian models, for which a closed expression of the exact P is known. The models are the conditional probability chain (CP) presented by Verstratte and Frankenberg,[9] and the zigzag chain (ZZ) or broken rod.[10]

For a polymer chain consisting of N elements sepa-

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(1) A preliminary report of this work was presented at the XIV Meeting of the Spanish Society of Physics and Chemistry, Sevilla, Oct 1969.

(2) A gaussian distribution does not necessarily imply the random-flight proportionality between $\langle r_{ij}^2\rangle$ and $|i - j|$. An example of gaussian distribution with more complicated second moment is given by A. Horta, *Eur. Polym. J.*, in press.

(3) A. J. Hyde, J. H. Ryan, and F. T. Wall, *J. Polym. Sci.*, **33** 129 (1958).

(4) O. B. Ptitsyn and Y. Y. Eisner, *Vysokomol. Soedin.*, **1**, 966 (1959).

(5) A. Peterlin in "Electromagnetic Scattering," M. Kerker, Ed., Pergamon Press, New York, N. Y., 1963, p 357.

(6) A. Peterlin, *Makromol. Chem.*, **9**, 244 (1953).

(7) P. J. Flory and R. L. Jernigan, *J. Amer. Chem. Soc.*, **90**, 3128 (1968).

(8) K. Nagai, *J. Chem. Phys.*, **38**, 924 (1963).

(9) G. Verstratte and C. v. Frankenberg, *J. Polym. Sci., Part A-2*, **5**, 1313 (1967).

(10) J. E. Hearst and W. H. Stockmayer, *J. Chem. Phys.*, **37**, 1425 (1962).

rated by segments of length b, the two models are as follows. The ZZ model is formed by n rods of equal length Lb, connected by universal joints, such that each rod consists of L scattering elements ($nL = N$). In the CP model, the segments of the actual polymer are considered to be part of a much larger hypothetical chain formed by random segments and subject to the condition of having a fixed elongation. The amount of this elongation is measured by a parameter f, which is zero for a random coil and one for a rigid rod (the detailed definition of the model is to be found in ref 9).

These two models are strong idealizations of a polymer molecule, but the reason for choosing them is clear: they are the only ones for which the exact P is known, and a determination of the numerical difference between this exact P and the gaussian approximation (obtained by substituting $\langle r_{ij}^2\rangle$ of the model into eq 2), is thus possible.

In the CP model, the correct calculation yields for P[9]

$$P = \frac{2}{a}\left\{\arctan\left(\frac{a}{c}\right) + \mathrm{Im}E_1(c + ia) + \frac{a}{a^2 + c^2}\left[e^{-c}\left(\frac{c}{a}\sin a + \cos a\right) - 1\right]\right\} \quad (3)$$

where $a = Nbf\omega$, $c = Nb^2\omega^2/6$, and $E_1(z)$ is the complex exponential integral.[11] The form of $\langle r_{ij}^2\rangle$ for this model is

$$\langle r_{ij}^2\rangle = b^2|i - j|(1 + f^2|i - j|) \quad (4)$$

which, substituted in (2), yields for the gaussian approximation P'

$$P' = \frac{(6\pi)^{1/2}}{a}\exp\left(\frac{3c^2}{2a^2}\right)\left(1 + \frac{3c}{a^2}\right) \times \left[\mathrm{erf}\left(\left(\frac{3}{2}\right)^{1/2}\frac{c}{a} + \frac{a}{6^{1/2}}\right) - \mathrm{erf}\left(\left(\frac{3}{2}\right)^{1/2}\frac{c}{a}\right)\right] + \frac{6}{a^2}\left[\exp\left(-c - \frac{a^2}{6}\right) - 1\right] \quad (5)$$

where erf(x) means error function.[11] Equation 5 has been already presented by Peterlin[5] and by Koyama,[12] but referred to different models than the one here considered. Peterlin deduces eq 4 from a model chain in which the segments have a constant average correlation $\langle\cos(ij)\rangle = \gamma$. For such a chain, $\langle r_{ij}^2\rangle$ is given by (4) if one identifies $2\gamma = f^2$. Koyama also uses eq 4 for $\langle r_{ij}^2\rangle$ and his derivation resembles a little more the CP model, because he considers a polymer chain conditioned to have a certain value of its radius of gyration. Both Peterlin and Koyama further assume that the form of P is gaussian, and they arrive at eq 5.

For the ZZ model, the correct calculation gives[13]

$$P = \frac{2}{n\rho}\left\{\mathrm{Si}(\rho) - \frac{2}{\rho}\sin^2\frac{\rho}{2} + \frac{[\mathrm{Si}(\rho)]^2}{\rho - \sin\rho}\left[1 - \frac{1 - \left(\dfrac{\sin\rho}{\rho}\right)^n}{n\left(1 - \dfrac{\sin\rho}{\rho}\right)}\right]\right\} \quad (6)$$

where $\rho = bL\omega$, and Si(x) is the sine integral.[11] The form of $\langle r_{ij}^2\rangle$ for this model reads

$$\langle r_{ij}^2\rangle = \begin{cases} b^2(i - j)^2 \\ \quad i \text{ and } j \text{ on the same rod} \\ b^2(i^2 + j^2 + rL^2) \\ \quad i \text{ on rod } t \text{ and } j \text{ on rod } t + r + 1 \ (r \geq 0) \end{cases} \quad (7)$$

Substitution of (7) into eq 2 yields the gaussian approximation P'

$$P' = \frac{(6)^{1/2}}{n\rho}\left\{(\pi)^{1/2}\mathrm{erf}\left(\frac{\rho}{6^{1/2}}\right) - \frac{(6)^{1/2}}{\rho}(1 - e^{-\rho^2}/6) + \frac{\pi(6)^{1/2}\left[\mathrm{erf}\left(\dfrac{\rho}{6^{1/2}}\right)\right]^2}{2\rho(1 - e^{-\rho^2}/6)}\left[1 - \frac{1 - e^{-n\rho^2}/6}{n(1 - e^{-\rho^2}/6)}\right]\right\} \quad (8)$$

The results for the particle scattering factor are conveniently discussed in terms of the variable χ defined by $\chi = \omega^2\langle R^2\rangle$, where $\langle R^2\rangle$ stands for the mean square radius of gyration. $\langle R^2\rangle = (n - 1 + 1/2n)b^2 \cdot L^2/6$ in the ZZ model,[13] and $\langle R^2\rangle = (1 + S)Nb^2/6$ in the CP model,[9] where the parameter S is defined as $S = Nf^2/2$. The arguments a and c in eq 3 and 5 transform to χ and S as $c = \chi/(1 + S)$ and $a = (12Sc)^{1/2}$. In the same way, ρ in eq 6 and 9 can be written in terms of χ and n as $\rho = [6\chi/(n - 1 + 1/2n)]^{1/2}$.

The results for the exact P and its gaussian approximation P', as functions of χ, are shown in Figure 1A (ZZ model) and Figure 1B (CP model) for several values of S and n. The curves represent the reciprocal scattering factor calculated according to eq 3, 5, 6, and 8.[14]

The difference between P and P' is obviously zero for the random coil, and it gradually increases as the value of P approaches that for a rigid rod. In both models $1/P'$ is *smaller* than $1/P$, which means that the approximate formulas are more sensitive to the degree of extension of the chain than the exact ones. A similar result was found by McIntyre, *et al.*,[15] who showed that the influence on P of excluded volume (represented by a power law) is less pronounced with the exact form of their distribution function (which is based on computer experiments of self-avoiding random walks on a lattice), than with the corresponding gaussian form.

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[11] As defined in "Handbook of Mathematical Functions," M. Abramowitz and I. A. Stegun, Ed., National Bureau of Standards, Washington D. C., 1964.

[12] R. Koyama, *J. Phys. Soc. Jap.*, **26**, 493 (1969).

[13] J. Hermans and J. J. Hermans, *J. Phys. Chem.*, **62**, 1543 1958).

[14] For $S = 0.5$ (CP model), direct integration of eq 2 (sums replaced by integrals) with $\langle r_{ij}^2\rangle$ given by (4) has been used instead of eq 6.

[15] D. McIntyre, J. Mazur, and A. M. Wims, *J. Chem. Phys.*, **49**, 2887 (1968).

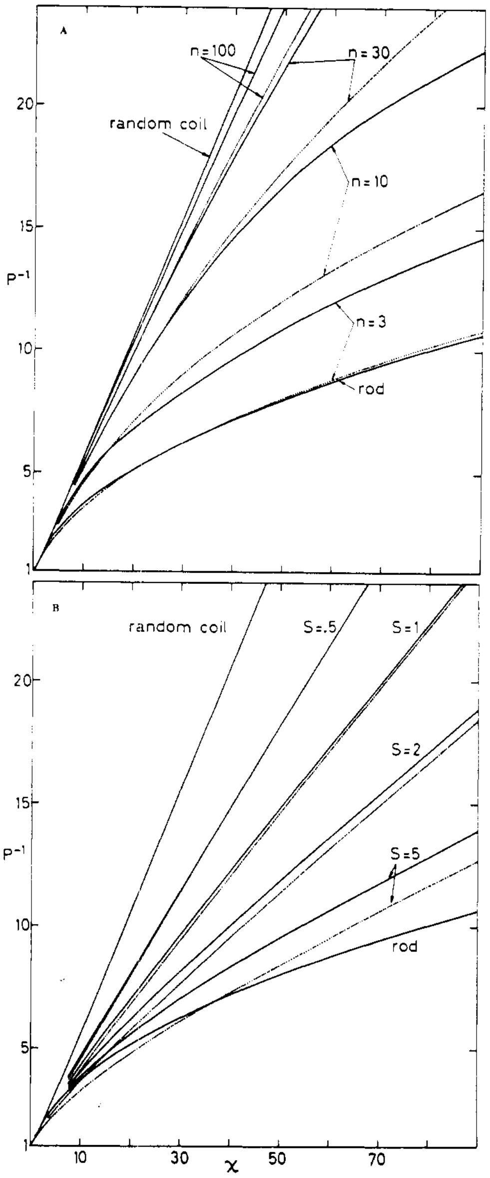

Figure 1. Reciprocal scattering factor for (A) model ZZ; (B) model CP: ———, values of the exact $1/P$; ······, values of the gaussian approximation $1/P'$.

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]

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(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

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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 $\mathbf{R}$ (or the radius of gyration S)[1,2]

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

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]

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

with

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

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

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.

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

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