$$= (1/4)\int_0^\infty [(3-\sigma)\cos(\sigma y - 2y) + 2\sigma\cos(\sigma y) - (3+\sigma)\cos(\sigma y + 2y)]y^{-1}\sin y\, dy$$

$$\begin{aligned} &= \pi\sigma/4, && 0 \leqslant \sigma \leqslant 1 \\ &= \pi(3-\sigma)/8, && 1 \leqslant \sigma \leqslant 3 \\ &= 0, && \sigma \geqslant 3 \end{aligned} \qquad (4)$$

Equations 3 and 4, when substituted into Eq. 1, lead to Eqs. VIII-36 and VIII-37.

Partial integration of Eq. 2 in the same manner as above yields for any value of n

$$I_n(\sigma) = (n-2)^{-1}\int_0^\infty [\sigma\cos\sigma y \sin y + n\sin\sigma y\cos y]y^{-(n-2)}\sin^{n-1} y\, dy$$

$$= [2(n-2)]^{-1}\int_0^\infty [(n+\sigma)\sin(\sigma y + y) + (n-\sigma)\sin(\sigma y - y)] \times y^{-(n-2)}\sin^{n-1} y\, dy$$

Hence

$$2(n-2)I_n(\sigma) = (n+\sigma)I_{n-1}(\sigma+1) + (n-\sigma)I_{n-1}(\sigma-1) \qquad (5)$$

The solution of this recursion relation is

$$I_n(\sigma) = (\pi/4)n(n-1)\sum_{t=0}^{\tau}\left[\frac{(-1)^t}{t!(n-t)!}\right]\left[\frac{n-\sigma-2t}{2}\right]^{n-2} \qquad (6)$$

where

$$(n-\sigma-2)/2 \leqslant \tau < (n-\sigma)/2$$

This result may be confirmed by substitution of Eq. 6 into Eq. 5. Verification, though tedious, is straightforward. Equation 6, when substituted into Eq. 1, gives Treloar's[1] equation, Eq. VIII-39. The correspondence of his result to the equation of Lord Rayleigh,[2] Eq. VIII-33, is thus established.

REFERENCES

1. L. R. G. Treloar, *Trans. Faraday Soc.*, 42, 77 (1946); see also *The Physics of Rubber Elasticity*, 2nd ed., Oxford Univ. Press, 1958, p. 97 *et seq.*
2. Lord Rayleigh, *Phil. Mag.* [6], 37, 321 (1919).

APPENDIX G

The Porod-Kratky Chain[1,2]

This hypothetical model for a chain molecule incorporates the concept of continuous curvature of the chain skeleton, the direction of curvature at any point of the trajectory being random.[1,2] It is frequently referred to as the worm-like chain. The model has had particular appeal for representing stiff chains, but its use has not been restricted to them alone.

The freely rotating chain, comprising bonds joined at fixed angles θ, serves as the starting point for definition of the Porod-Kratky chain. The Porod-Kratky chain is more closely related to the freely rotating chain than to others treated in detail in the text. The average projection of the kth bond of a freely rotating chain on the direction of the first bond is $l'\alpha^{k-1}$, where l' is the bond length and $\alpha = \cos\theta'$, with θ' denoting the fixed angle between successive bonds. Primes are used in order to distinguish bonds and bond angles of the freely rotating, model chain from the corresponding quantities for the real chain it is intended to represent. The average sum of projections of n' of these bonds on the direction of the first bond is[1,2]

$$\overline{X}_1 = \mathbf{r}\cdot(\mathbf{l}_1/l_1) = l'\sum_{k=0}^{n'-1}\alpha^k \qquad (1)$$

where $\mathbf{l}_1/l_1$ is the unit vector on the first bond.

If the chain is made indefinitely long, then $\overline{X}_1$ becomes the *persistence length* defined in Chapter IV (see p. 111) as the sum of the average projections of all bonds $i = 1$ to ∞ on the direction of the first bond. Denoting the persistence length by a, we have from Eq. 1

$$a = l'/(1-\alpha) \qquad (2)$$

The persistence length for a real chain is determined by its structure and by hindrances to bond rotations. It is directly related to the characteristic ratio C_∞ (see Eq. IV-48).

Let the freely rotating chain of finite length considered above be subdivided into shorter and shorter bonds in such a way as to maintain the constancy of the *contour length* L and of the persistence length a at their predetermined values. Continuation of the subdivision to the limit $l' = 0$ and $n' = \infty$ yields the Porod-Kratky[1,2] chain of continuously varying direction. In this limit $1 - \alpha$ also vanishes, and it does so in the manner required by Eq. 2 to maintain a at its specified value. Equation 2 may be replaced by

$$a = \lim_{l' \to 0} (-l'/\ln \alpha) \tag{3}$$

Through the introduction of a thus defined into Eq. 1, we obtain

$$\overline{X}_1 = l' \sum_{k=0}^{n'-1} \exp(-kl'/a) \tag{4}$$

$$= \int_0^L \exp(-K/a)\, dK \tag{5}$$

$$= a[1 - \exp(-L/a)] \tag{6}$$

with $L = n'l'$.

Replacement of $\overline{X}_1$ by $\langle r^2 \rangle_0$ as the relevant variable may be accomplished by relating differential quantities as follows[1,2]:

$$d\langle r^2 \rangle_0 = 2\langle \mathbf{r} \cdot d\mathbf{r} \rangle = 2\overline{X}_1\, dL \tag{7}$$

The latter relation may be verified readily by considering the increment dL to be added at the beginning of the chain. Then the magnitude of $d\mathbf{r}$ is dL and its direction coincides with X_1. Equation 7 follows at once. Substitution of Eq. 6 for $\overline{X}_1$ into Eq. 7 and integration yields[1,2]

$$\langle r^2 \rangle_0/L = 2a[1 - (a/L)(1 - e^{-L/a})] \tag{8}$$

In the limit $L \to \infty$

$$(\langle r^2 \rangle_0/L)_\infty = 2a \tag{9}$$

Thus, the representation of the hypothetical Porod-Kratky model chain depends on two parameters a and L. In order to proceed further, it is necessary to establish a correspondence between these quantities and characteristics of the real chain. This step is attended by a degree of arbitrariness. A reasonable course is the following. Let L be identified with the length r_{max} of the real chain when fully extended. The ratio L/nl is thereby established. Note that $L = r_{max}$ is less than nl, in general, owing to valence angle restrictions, these angles being assumed to be fixed.* Second, we so choose a as to establish coincidence between C_∞ for the model and for the real chain. Thus, the limiting value of the characteristic ratio for the model chain is given according to Eq. 9 by

$$C_\infty \equiv (\langle r^2 \rangle_0/nl^2)_\infty = (L/nl)(2a/l) \tag{10}$$

*The specification of L in this manner is not without complications in some cases. If valence angles θ differ for successive skeletal atoms, then the most highly extended conformation may be nonplanar and its precise geometrical description is not immediately obvious.

where l and n are the bond length and number of bonds, respectively, for the *real* chain.* The Porod-Kratky relation, Eq. 8, for the second moment of $\mathbf{r}$ may be expressed in like terms as follows:

$$\langle r^2 \rangle_0/nl^2 = C_\infty[1 - (L/a)^{-1}(1 - e^{-L/a})] \tag{11}$$

where L is understood to be related to n according to Eq. 10.

For short chains, or very stiff ones, Eq. 8 may be expanded in the following series:

$$\langle r^2 \rangle_0/L = L[1 - (1/3)(L/a) + (1/12)(L/a)^2 - \cdots], \qquad (L/a) < 1 \tag{12}$$

For long, or "flexible," chains

$$\langle r^2 \rangle_0/L \cong 2a[1 - (L/a)^{-1}], \qquad (L/a) \gg 1 \tag{13}$$

or

$$\langle r^2 \rangle_0/nl^2 \cong C_\infty[1 - (L/a)^{-1}], \qquad (L/a) \gg 1 \tag{14}$$

In this limit, the characteristic ratio is linear in L^{-1}, or in n^{-1}.

Expressions for the fourth and sixth moments of $\mathbf{r}$ for the Porod-Kratky chain have been derived by Hermans and Ullman[3] and by Heine, Kratky, and Porod.[4] Benoit and Doty[5] have derived the following expression for the unperturbed radius of gyration of this model chain:

$$\langle s^2 \rangle_0/L = (a/3)\{1 - (3a/L)[1 - 2(a/L) + 2(a/L)^2 - 2(a/L)^2 e^{-L/a}]\} \tag{15}$$

or

$$\langle s^2 \rangle_0/nl^2 = (\langle s^2 \rangle_0/nl^2)_\infty[1 - 3(a/L) + 6(a/L)^2 - 6(a/L)^3(1 - e^{-L/a})] \tag{16}$$

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4. S. Heine, O. Kratky, and G. Porod, *Makromol. Chem.*, **44**, 682 (1961).
5. H. Benoit and P. Doty, *J. Phys. Chem.*, **57**, 958 (1953).

*According to Eq. IV-48

$$(\langle r^2 \rangle_0/nl^2)_\infty = (2a - l)/l$$

for a real chain. This expression differs, of course, from that for the Porod-Kratky model chain as expressed by Eq. 10. The difference arises in part from the inclusion of the first step (bond) of the real chain which by definition is coincident with the direction of $\overline{X}_1$.

APPENDIX H

The Average Orientation of a Vector within a Chain of Specified End-to-End Vector r

The following analysis[1] is addressed to a molecular chain whose end-to-end vector **r** is specified within a laboratory reference frame XYZ. The "molecule" under consideration may, for example, be the portion of a network extending from one cross-linkage to the next, as is explained more fully in Chapter IX, Section 3. In any event, the chain is subject only to the constraint imposed by stipulation of the vector **r** separating its ends.

We focus attention on a unit vector $\mathbf{v}_{it}$ affixed to the ith skeletal bond or unit. If this vector is identified with the direction of one of the principal components of the optical polarizability tensor $\boldsymbol{\alpha}$, the results here obtained are applicable to analysis of the strain birefringence (see Chap. IX, Sect. 3). Identification of $\mathbf{v}_{it}$ with the transition moment for excitation of group i by absorption of radiation of a given wavelength provides the basis for treatment of the dichroic ratio. Finally, the preferential orientation of a given bond by extension of the chain may be obtained by identifying the unit vector with the direction of the bond. Whatever the identification of $\mathbf{v}_{it}$ may be, we seek the average square of its projection on chain vector **r** as a function of r. The relationship will be obtained as a series in even powers of r, by resort to a procedure developed by Nagai.[1]

Letting $(\mathbf{v}_{it}, \mathbf{X})$ denote the cosine of the angle between $\mathbf{v}_{it}$ and axis X of the fixed reference frame, we have

$$\langle(\mathbf{v}_{it}, \mathbf{X})^2\rangle_r = \tilde{Z}_r^{-1}\int \cdots_{\mathbf{r}} \int (\mathbf{v}_{it}, \mathbf{X})^2 \exp(-E/kT) \sin\chi\, d\chi\, d\psi\, d\omega\, d\{\phi\}/8\pi^2\, d\mathbf{r} \tag{1}$$

where $\tilde{Z}_r$ is the configuration partition function for a chain of specified **r** (see Eq. VIII-2); χ, ψ, and ω are Eulerian angles, and $\{\phi\}$ is the set of internal, skeletal bond rotations; these and other symbols carry the definitions given in Chapter VIII, Section 1.

The Fourier transform of the integral in Eq. 1 is

$$\begin{aligned} H_{it}(\mathbf{q}) &= \int e^{\bar{\imath}\mathbf{q}\cdot\mathbf{r}} \tilde{Z}_r \langle(\mathbf{v}_{it}, \mathbf{X})^2\rangle_r\, d\mathbf{r} \\ &= (8\pi^2)^{-1} \int \cdots \int (\mathbf{v}_{it}, \mathbf{X})^2 \exp(-E/kT) \exp(\bar{\imath}\mathbf{q}\cdot\mathbf{r}) \\ &\quad \times \sin\chi\, d\chi\, d\psi\, d\omega\, d\{\phi\} \end{aligned} \tag{2}$$

Pursuant to the evaluation of this expression, it will be helpful to define a new Cartesian coordinate system, xyz, with the z axis taken parallel to vector **q**, and the x axis in the Xz plane; the direction of the x axis will be chosen to make an acute angle with X. The Eulerian angles are conveniently defined as in Fig. 1. That is, χ and ψ are the polar and azimuthal angles, respectively, locating **r** with reference to **q** (i.e., z) as the polar axis; ω measures the rotation of the plane defined by $\mathbf{v}_{it}$ and **r** from the plane of **r** and z. Further, let Φ_{it} be the angle made by $\mathbf{v}_{it}$ with **r**, and let τ denote the angle between **q** and the fixed axis X (not shown in Fig. 1), i.e.,

$$\cos\tau \equiv (\mathbf{q}, \mathbf{X}) = q_1/q \tag{3}$$

where q_1 is the projection of **q** on X, and $q = |\mathbf{q}|$. Then a unit vector along the X axis is expressed in the coordinate system xyz by

$$\mathbf{X}/X = \begin{bmatrix} \sin\tau \\ 0 \\ \cos\tau \end{bmatrix} \tag{4}$$

The unit vector $\mathbf{v}_{it}$ expressed in the same coordinate system is

$$\mathbf{v}_{it} = \begin{bmatrix} \sin\chi\cos\psi\cos\Phi_{it} + (\cos\chi\cos\psi\cos\omega - \sin\psi\sin\omega)\sin\Phi_{it} \\ \sin\chi\sin\psi\cos\Phi_{it} + (\cos\chi\sin\psi\cos\omega + \cos\psi\sin\omega)\sin\Phi_{it} \\ \cos\chi\cos\Phi_{it} \qquad - \sin\chi\cos\omega\sin\Phi_{it} \end{bmatrix} \tag{5}$$

The cosine of the angle between these two unit vectors is

$$\begin{aligned} (\mathbf{v}_{it}, \mathbf{X}) &= \sin\tau[\sin\chi\cos\psi\cos\Phi_{it} + (\cos\chi\cos\psi\cos\omega - \sin\psi\sin\omega)\sin\Phi_{it}] \\ &\quad + \cos\tau[\cos\chi\cos\Phi_{it} - \sin\chi\cos\omega\sin\Phi_{it}] \end{aligned} \tag{6}$$

Substitution of Eq. 6 into Eq. 2 and integration over the Eulerian angles at fixed internal configuration $\{\phi\}$ leads to

$$\begin{aligned} H_{it}(\mathbf{q}) &= \frac{1}{3}\int \cdots \int \left\{\frac{\sin qr}{qr} + \left(\frac{1}{2}\right)(3\cos^2\tau - 1)(3\cos^2\Phi_{it} - 1)\right. \\ &\quad \left. \times \left[\frac{\sin qr}{qr} + \frac{3\cos qr}{(qr)^2} - \frac{3\sin qr}{(qr)^3}\right]\right\} e^{-E/kT}\, d\{\phi\} \qquad (7) \\ &= \frac{1}{3}\int \cdots \int \left\{\left[1 - \frac{(qr)^2}{3!} + \frac{(qr)^4}{5!} - \frac{(qr)^6}{7!} + \cdots\right]\right. \end{aligned}$$