``Volume Effect'' and Random Flights

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latter parameter is a constant for each homologous series and is equal to $A_m=\bar{h}^2/L$, $\bar{h}^2$ being the mean square distance between the ends of the chain).

Equations (3), (3a) include the two aforementioned limiting cases. For instance, in the case of large values of Z, it transforms to

$$\mathbf{K}=\eta_0 Lu\bigg/\left(0.1\left(\frac{L}{A_m}\right)^{\frac{1}{2}}\right)=10\eta_0(LA_m)^{\frac{1}{2}}=10\eta_0(\bar{h}^2)^{\frac{1}{2}}u,$$

which is approximately equal to the resistance $\mathbf{K}=3\pi\eta_0(\bar{h}^2)^{\frac{1}{2}}u$ of a compact sphere of diameter equal to the average diameter of the coil (complete immobilization).

From Eqs. (3), (3a) can easily be obtained the following expressions for the sedimentation constant s and for the diffusion constant D[5, ††]

$$s=a_1+b_1(Z)^{\frac{1}{2}}, \tag{4}$$

$$D=(a_2+b_2(Z)^{\frac{1}{2}})\frac{1}{Z}, \tag{5}$$

where the constants

$$a_1=\frac{M_g}{N_L b}\frac{1-v_{\text{part}}\rho_0}{\eta_0}\left(0.02+0.16\log^{10}\frac{A_m}{d_h}\right), \tag{4a}$$

$$b_1=\frac{M_g}{N_L b}\frac{1-v_{\text{part}}\rho_0}{\eta_0}0.1\left(\frac{b}{A_m}\right)^{\frac{1}{2}}, \tag{4b}$$

$$a_2=\frac{kT}{\eta_0 b}\left(0.02+0.16\log^{10}\frac{A_m}{d_h}\right), \tag{5a}$$

$$b_2=\frac{kT}{\eta_0 b}0.1\left(\frac{b}{A_m}\right)^{\frac{1}{2}} \tag{5b}$$

are independent upon the degree of polymerization Z. N_L is Loschmidt's number, M_g the molecular weight of the monomer unit, v_{part} the partial specific volume of the solute, ρ_0 the density of the solvent, k Boltzmann's constant, T the absolute temperature, and b the hydrodynamic length of the monomer unit (b is related to the hydrodynamic length L of the chain by the expression $L=b\cdot Z$). Equations (4) and (5) are found to be verified by the empirical data.

The partial immobilization is as important for rotational as for translational motions of the coil. Rotational experiments on models have shown that the rotational resistance and thus the rotational diffusion constant of random coils are given by simple expressions [analogous to (3), (3a)] as functions of A_m, d_h, and L.[5]

The motion of a particle suspended in a liquid with flow gradient is a translation superimposed by a rotation of the particle; therefore the rotational diffusion constant determines to a large extent the birefringence of flow and the viscosity of the solution.[3, 7]

By introducing the result of our rotational experiments on models into our earlier equation,[4] we obtain for the intrinsic viscosity[6, 8]

$$\frac{\eta_{sp}}{c}=\frac{A_m b^2}{48}\frac{N_L}{10^3}\frac{Z}{-0.05+0.12\log^{10}\dfrac{A_m}{d_h}+0.037\left(\dfrac{bZ}{A_m}\right)^{\frac{1}{2}}}\ddagger,\ddagger\ddagger \tag{6}$$

(c concentration in base moles per liter).

The orientation and the value of the birefringence of flow can equally be described by expressions that take into account the partial immobilization of liquid inside the coil.[6]

P. Debye[11] and H. C. Brinkman[12] have recently also recognized the importance of partial immobilization on the viscosity, apparently without knowledge of our investigations in this field. The considerations of these authors are, as far as they have come to our knowledge, very similar to our own and represent to a considerable extent another expression of the same results. Thus the introduction of a "shielding ratio" by Debye corresponds entirely to our partial immobilization, and the cases (1) and (2) discussed in 1943 have again been found by Debye. Our expressions have the advantage of containing parameters that are determined by experiments on models, while the corresponding parameters of these authors refer to a non-realized spherical shape of the coils considered.

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* Reference 4, p. 1398.
** Reference 4, p. 1397.
*** Reference 4, p. 1443–44.
† Reference 4, p. 1420–21.
†† The linear relationship between the sedimentation constant and the square root of the degree of polymerization has already been recognized in our 1943 paper (reference 4, p. 1398).
‡ Equation (6) has been used already in reference 9, p. 85 and 92, reference 10, pp. 1573 and 1577.
‡‡ Reference 8 contains equally the corresponding quantitative expressions for branched chain molecules.

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"Volume Effect" and Random Flights

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THE so-called "volume effect" in flexible high polymer molecules has been a troublesome feature of high polymer theory since 1934.[1–3]

This note is to point out that the effect may be computed by elementary methods. In the random flight notation of Chandrasekhar[4] the probability of a flight of N randomly directed unit vectors from (x_1, y_1, z_1) to (x_2, y_2, z_2) (vector r_{12}) is

$$W_N(r_{12})dx_2dy_2dz_2=(2\pi^2|r_{12}|)^{-1}\int_0^\infty \sin(|\lambda||r_{12}|)\times(\sin|\lambda|/|\lambda|)^N|\lambda|d|\lambda|dx_2dy_2dz_2.$$

We write this in terms of the coordinates and abbreviate somewhat to

$$W_N(r_{12})dx_2dy_2dz_2=W_N(x_1, x_2)dx_2.$$

A path from point 1 to point 2 in N steps is denoted **1N2**.

Now the probability of a path of $S=L+M+N$ steps, **0L1M2N3**, is

$$W_L(0, x_1)W_M(x_1, x_2)W_N(x_2, x_3)dx_1dx_2dx_3.$$

If the total number of steps S is fixed, then the middle section of M steps may range from the least integer greater than the distance from point 1 to point 2, denoted $\bar{r}_{12}$ up to $S-\bar{r}_{01}-\bar{r}_{23}$, where all the slack between 0 and 1 and 2 and 3 is taken up, and similarly for the other segments.

The probability of one of these events is (if $i+j+k=S$)

$$\sum_{i=\bar{r}_{01}}^{S-\bar{r}_{12}-\bar{r}_{23}} \sum_{j=\bar{r}_{12}}^{S-\bar{r}_{01}-\bar{r}_{23}} \sum_{k=\bar{r}_{23}}^{S-\bar{r}_{01}-\bar{r}_{12}} W_i(0, x_1)W_j \times (x_1, x_2)W_k(x_2, x_3)dx_1dx_2dx_3.$$

Now if point 1 and point 2 are within a certain critical distance of each other, we have what may be called a "loop" of vectors. A loop cannot occur if the vectors are the line of centers of a solid molecule.

If the last expression is integrated with respect to x_2, y_2, z_2 throughout a sphere of radius a centered at x_1, y_1, z_1 we have the probability that a loop of some size is formed.

This may be written

$$\int_{a_1x_2} \Sigma_{i_1j_1k}\, W_i(0, x_1)W_j(x_1, x_2)W_k(x_2, x_3)dx_1dx_2dx_3.$$

In the exact sense point 1 may be anywhere within a near-ellipsoidal solid of revolution with "foci" at points 1 and 3. If suitable asymptotic values are used point 1 may be anywhere. In either case, we integrate over the available range. This supplies the probability that at least one loop occurs somewhere on the path from 1 to 3. The complement to this is the probability that none occur. This is

$$\left\{W_S(0, x_3)-\int_{\infty,\, x_1}\int_{a_1x_2} \Sigma_{i_1j_1k}\, W_i(0, x_1)W_j \times (x_1, x_2)W_k(x_2, x_3)dx_1dx_2\right\}dx_3.$$

Details and applications to items in high polymer physics are being prepared.

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Free Electron Model for Absorption Spectra of Organic Dyes

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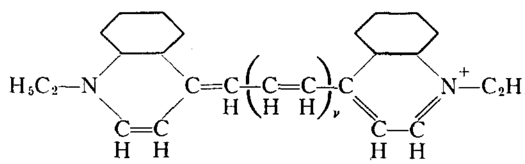
A PAPER by N. S. Bayliss,[1] in which the absorption of polyenes is treated by a free electron model, has appeared recently in this Journal; the π-electrons belonging to the double bonds are assumed to have free mobility along the conjugated chain and to behave as a one-dimensional Fermi gas in a field of uniform potential energy. This model predicts values much too small of the wave-lengths of the absorption bands of polyenes; for instance, in carotene, according to Bayliss, the theoretical and experimental values of the wave-length of the first absorption band are 9700A and 4540A, respectively.

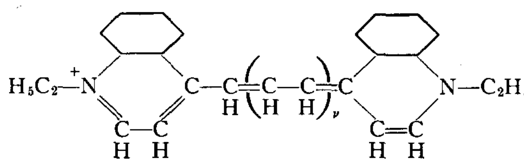
This discrepancy follows from the fact that in the ground state of a polyene molecule the π-electron gas just fills its first Brillouin zone, a zone which is produced by a periodicity of the potential energy along the chain due to the alternating "single" and "double" bonds. The electron jump corresponding to the first absorption band is a jump from the top of the first to the bottom of the second Brillouin zone; this process requires much more energy and, consequently, the absorption band appears at a much shorter wave-length than one would expect by a free electron model.

It has been shown recently[2] that a one-dimensional free electron gas model is, however, an appropriate approximation for a quantitative study of the absorption of a number of other colored substances, such as symmetric carbocyanine dyes, where the two resonating structures of the cation,



(Ia)

and



(Ib)

are equivalent. All C—C distances along the chain are equal, and the periodicity of "single" and "double" bond distances, which causes the appearance of the aforementioned Brillouin zone in the case of polyenes, is absent here.[3] There is a half-filled energy band in the ground state of the π-electron gas, and the electron jump corresponding to the first absorption band is a jump from the highest filled level to the next empty one. As these two levels are in the middle of an energy band, a free electron model is expected to give a reasonable approximation for their separation energy and consequently for the position of the peak of the corresponding absorption band.

Let us designate by Z the number of atoms that are linearly connected to the chain of resonating single and double bonds, and by l the bond distance between two neighbors of the chain. (In the case of a cyanine dye of structure (Ia), (Ib), where there is a chain of resonating single and double bonds between the two nitrogen atoms, Z is equal to $2\nu+9$ [see structure (Ia), (Ib)], and l is equal to 1.39×10^{-8} cm [i.e., equals the C—C distance in benzene].) The π-electrons are assumed to have free mobility along the zigzag chain of resonating single and double bonds (with inclusion of the area of the two nitrogen atoms at each end), i.e., along a line of total length $L=l(Z+1)$. The energy of the nth quantum state of this one-dimensional electron gas is then given by the expression[4]

$$E_n=\frac{h^2n^2}{8mL^2}=\frac{h^2n^2}{8ml^2(Z+1)^2}, \tag{1}$$