

AD No. 17232  
ASTIA FILE COPY

OFFICE OF NAVAL RESEARCH

CONTRACT N5ori-076

T. O. 54

NR-330-025

"CHARACTERIZATION OF CELLULOSE AND POLYPEPTIDE POLYMERS"

Paul Doty

Technical Report No. 3

Part III

"DEPOLARIZATION OF THE LIGHT SCATTERED BY SOLUTIONS OF MACROMOLECULES"

H. Benoit

Gibbs Memorial Laboratory

Harvard University

Cambridge, Massachusetts

August 7, 1953

### Part III

## DEPOLARIZATION OF THE LIGHT SCATTERED BY SOLUTIONS OF MACROMOLECULES\*

H. Benoit

Gibbs Memorial Laboratory, Harvard University, Cambridge, Massachusetts

\* Appeared in Compt. rend. 236, 687 (1953)

I. Let us suppose we have a molecule made up of  $N$  identical elements, each of which can be considered as a Langevin molecule. We call  $\alpha$  and  $\beta$  the principal polarizabilities and  $\delta_0 = (\alpha - \beta)/(\beta + 2\beta)$  its anisotropy.

We want to evaluate the depolarization of the light scattered by a system formed by a large number of molecules of this type. For this purpose we use a Cartesian system of coordinates with the vertical axis  $OZ$  and  $OX$  in the direction of the incident beam,

The orientation of the  $i$ th element of the molecule is characterized by its direction cosines  $\lambda_i \mu_i \nu_i$ . Assuming that the dimensions of the molecule are small in comparison to the wavelength of the light, the use of Cabannes' formulas<sup>1</sup> gives for the three classical components

$$V_v = K \sum_i \sum_j [\beta + (\alpha - \beta) \nu_i^2] [\beta + (\alpha - \beta) \nu_j^2]$$

$$V_h = K \sum_i \sum_j (\alpha - \beta)^2 \mu_i \nu_i \mu_j \nu_j$$

$$H_h = K \sum_i \sum_j \frac{[(\alpha - \beta) \mu_i \lambda_i \sin \omega - \beta - (\alpha - \beta) \nu_i^2 \cos \omega] [(\alpha - \beta) \lambda_j \mu_j \sin \omega - \beta - (\alpha - \beta) \nu_j^2 \cos \omega]}{(\alpha - \beta) \nu_j^2 \cos \omega}$$

The double summation must be extended to all pairs of elements of the molecule,  $K$  is a proportionality coefficient, a function of the number of molecules, the wavelength of the light and the refractive index,

$\omega$  is the angle between the incident and the scattered beam. The averaging has to be performed over all configurations and orientations.

The result is easily obtained:

$$V_v = K' \sum_i \sum_j \left[ 1 + \frac{4}{5} \delta_o^2 \overline{p_{ij}} \right]$$

$$V_h = K' \frac{3}{5} \delta_o^2 \sum_i \sum_j \overline{p_{ij}}$$

$$H_h = V_v \cos^2 \omega + V_h \sin^2 \omega$$

where  $\overline{p_{ij}} = \frac{3 \cos^2 \varphi_{ij} - 1}{2}$ ,  $\varphi_{ij}$  being the angle between the axis and the ellipsoids of polarizability  $i$  and  $j$  and  $\omega$  is the angle between the incident and the scattered light. These formulas show that we can characterize a flexible molecule by its anisotropy  $\delta$  as in the case of rigid particles,  $\delta$  being given by the expression:

$$\delta^2 = \frac{\delta_o^2}{N} \sum_i \sum_j \overline{p_{ij}}$$

and the problem now is to evaluate  $\delta$  for different models.

## II. Calculation of $\delta$ for different models.

a) Gaussian chain. For this chain the orientation of the different elements are independent.

$$\overline{p_{ij}} = 0 \quad \text{for} \quad i \neq j$$

$$\overline{p_{ij}} = 1 \quad \text{for} \quad i = j \quad \text{and}$$

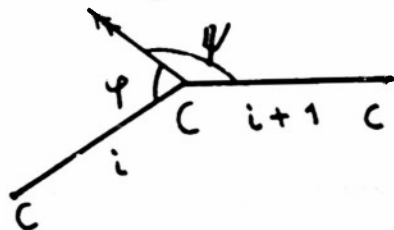
$$\delta^2 = \frac{\delta_o^2}{N} \quad \text{where } N \text{ is the number of statistical elements}$$

and  $\delta_o$  their anisotropy.

This result has already been obtained by Stuart and Peterlin<sup>2</sup> and Kuhn<sup>3</sup>.

b) Rod-like chain. All the elements are parallel and  $\overline{p_{ij}} = 1$  which gives  $\delta = \delta_0$ . His result has been obtained as a particular case by Horn, Benoit and Oster<sup>4</sup>.

c) Aliphatic chain with free rotations. We call  $\delta_0$  the anisotropy of one monomeric unit.  $\varphi$  is the angle formed by the axis of the ellipsoid of polarizability of the  $i$ th element with its C-C bond and  $\psi$  is the angle of the same axis with the  $i+1$  C-C bond.



Under these conditions:

$$\overline{p_{ij}} = \frac{3 \cos^2 \varphi - 1}{2} \frac{3 \cos^2 \psi - 1}{2} \left[ \frac{3 \cos^2 \theta - 1}{2} \right]^{|i-j| + 1}$$

where  $\theta$  is the supplement of the valence angle. Using this relation, one obtains for every value of  $N$

$$\delta^2 = \frac{\delta_0^2}{N} \left[ 1 + \frac{1}{2} (3 \cos^2 \varphi - 1)(3 \cos^2 \psi - 1) \frac{N(1-p) - 1 + p^N}{N(1-p)^2} \right]$$

$$\text{with } p = \frac{3 \cos^2 \theta - 1}{2}$$

More particularly, if the axis of the ellipsoid of polarizability has the direction of the C-C bond,  $\varphi = 0$ ,  $\psi = \theta$  and

$$\delta^2 = \frac{\delta_0^2}{N^2} \left[ N \frac{1+p}{1-p} - 2p \frac{1-p^N}{(1-p)^2} \right]$$

The bracket is similar to the Eyring expression for the end-to-end distance and differs only by the fact that  $\cos \theta$  is replaced by

$p = \frac{3 \cos^2 \theta - 1}{2}$ . This shows that the behavior of  $\frac{\langle r^2 \rangle}{N^2}$  is similar to the behavior of the mean square end-to-end distance. For instance, for long chain in the Gaussian range, we have

$$\langle r^2 \rangle = \frac{\langle r_0^2 \rangle}{N} \frac{1+p}{1-p}$$

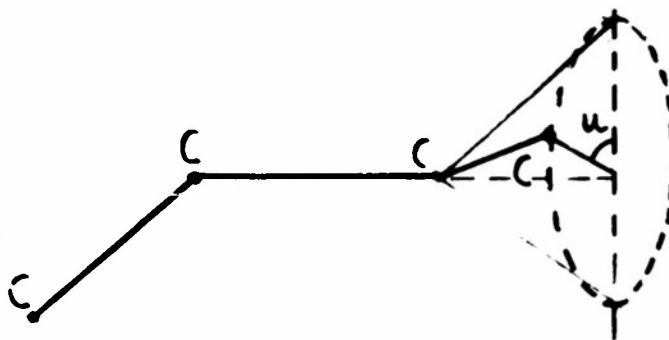
d) Aliphatic chain with steric and energetic hindrance. The method is similar to the one used by Debye and Hückel<sup>5</sup> for the calculation of the electric dipole moment of such a chain.

We assume that the rotation on the valence cone is not free and we characterize the lack of freedom by the following averages.

$$\cos u = q$$

$$\sin u = 0$$

$$\cos^2 u = r$$



With these assumptions it is possible to get a recurrence relation between  $p_{ij}$ ,  $p_{ij-1}$ , but this relation, which can be used for specific numerical calculations, does not allow us to give a general result in a simple closed form.

Here we give only the result for a long chain in the case where the direction of the ellipsoid of polarizability is the direction of the C-C bond.

$$\delta^2 = \frac{\delta_0^2}{N} \left[ 1 + \frac{2}{3} \frac{3(p+r)(1-q) + 2(q-r)(1+2p)}{(1-p)(1-r)} \right]$$

The behavior is not different from that observed in the preceding case.

These results are all obtained with the assumption that the chain is short in comparison to the wave length. If this is not the case, by extrapolating to zero angle between the incident and scattered beam, one can apply this formula, since the interference due to the size of the particle disappears at zero.

III. Application to the problem of fluid. In a liquid, or a compressed gas where the interactions are at short range compared to the wave-length, the same calculation can be used since it is only in the second part that we have used the fact that the units were parts of a macromolecular chain.

We assume that the polarizabilities  $\alpha$  and  $\beta$  are independent of the relative orientation of the molecule. Introducing the new function

$$p(r) = \frac{3 \cos^2 \varphi - 1}{2}$$

$\varphi$  being the angle of the axis of two ellipsoids of polarizability and  $\overline{\cos^2 \varphi}$  the average values at constant  $r$ , one can show that the depolarization,  $\delta$ , of the system is given by the formula:

$$\delta^2 = \delta_0^2 \frac{1 + \frac{4\pi N}{V} \int_0^\infty p(r) g(r) r^2 dr}{1 + \frac{4\pi N}{V} \int_0^\infty [1 - g(r)] r^2 dr}$$

where  $g(r)$  is the well-known radial distribution function and  $N$  the number of particles in the volume  $V$ . This formula which is similar to the Zernicke and Prins<sup>6</sup> formula can be used to describe the variation

of anisotropy with concentration in a solution, or with pressure in a gas, and perhaps to study the depolarization of liquids. It shows that the depolarization is a function of the radial distribution and of the relative orientation of the particles. Due to the form of the expansion,  $\delta$  can be larger or smaller than  $\delta_0$ , in other words the interaction can increase or decrease the value of the anisotropy and we plan to evaluate with this formula the second virial coefficient in the expansion of  $\delta^2$  as a function of the concentration for some simple dilute systems.

1. J. Cabannes, La diffusion de la lumiere, Paris, 1929
2. H. A. Stuart and A. Peterlin, J. Pol. Sci. 5, 543 (1950)
3. H. Kuhn, Helv. Chem. Acta. 29, 432 (1946)
4. P. Horn, H. Benoit and G. Oster, J. Chim. Phys. 48, 530 (1951)
5. P. Debye and F. Bueche, J. Chem. Phys. 19, 589 (1951)
6. F. Zernicke and J. A. Prins, Z. Physik 41, 184 (1927)