

## The Scattering of Light and the Radial Distribution Function of High Polymer Solutions

Bruno H. Zimm

Citation: *J. Chem. Phys.* **16**, 1093 (1948); doi: 10.1063/1.1746738

View online: <http://dx.doi.org/10.1063/1.1746738>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v16/i12>

Published by the [American Institute of Physics](#).

---

### Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: [http://jcp.aip.org/about/about\\_the\\_journal](http://jcp.aip.org/about/about_the_journal)

Top downloads: [http://jcp.aip.org/features/most\\_downloaded](http://jcp.aip.org/features/most_downloaded)

Information for Authors: <http://jcp.aip.org/authors>

## ADVERTISEMENT



**AIPAdvances**

Special Topic Section:  
**PHYSICS OF CANCER**

Why cancer? Why physics? [View Articles Now](#)

# The Scattering of Light and the Radial Distribution Function of High Polymer Solutions

BRUNO H. ZIMM

*Department of Chemistry, University of California, Berkeley, California*

(Received June 2, 1948)

A radial distribution function of polymer segments in a solution of a high polymer may be defined as a quantity proportional to the density of segments at a given distance from some given segment. An approximate expression is derived for this function for dilute solutions of chain molecules of moderate degrees of polymerization. By Fourier inversion a simple expression for the intensity of light scattering, as a function of angle and concentration, may be obtained.

## I. INTRODUCTION

THE following work describes briefly the theoretical derivation of some equations connected with the phenomenon of light scattering from solutions of thread-like molecules.\* The use of these equations in handling experimental data is described in a succeeding paper.

A radial distribution function,  $\rho(r)$ , for polymer segments in a polymer solution may be defined by the statement that  $nN\rho(r)d\tau/V$  is the probability of finding the center of some segment within the volume element  $d\tau$  at a distance  $r$  from some other arbitrarily chosen segment, given that there are  $N$  polymer molecules of  $n$  segments each in a total volume  $V$ . By "segment" is meant an arbitrary small portion of the chain of a thread-like molecule. In the ensuing discussion it will be assumed that all the segments in the solution have the same constitution and size, also that all molecules have the same degree of polymerization  $n$ .

When a dilute solution of such a nature is illuminated by a parallel beam of light, the excess scattering (over that of the solvent alone) will be given by the well-known formula,

$$I(\vartheta) = \frac{kn^2N^2}{V^2} \int \rho(r) \exp\left(\frac{2\pi i \mathbf{s} \cdot \mathbf{r}}{\lambda}\right) d\tau. \quad (1)$$

In this equation,  $I(\vartheta)$  is the intensity of excess scattering per cubic centimeter,  $\vartheta$  is the angle between the incident and scattered rays,  $\mathbf{s}$  the vector difference between unit vectors in the directions of the incident and scattered rays,

$\lambda$  the wave-length. The integration goes over all orientations as well as magnitudes of  $\mathbf{r}$  at constant  $\mathbf{s}$ . The magnitude of  $\mathbf{s}$  is found to be  $2 \sin(\vartheta/2)$ . The factor  $K$  contains the electromagnetic constants of the material and a function of the angle of scattering. If the incident light is unpolarized,  $K$  is proportional to  $1 + \cos^2\vartheta$ . If the incident beam is plane-polarized,  $K$  is proportional to  $\sin^2\varphi$ , where  $\varphi$  is the angle between the direction of scattering and the normal to the direction of the incident beam in the plane of vibration of the electric vector.

Aside from its intrinsic interest as a property of the solution, the radial distribution function  $\rho(r)$  has value, therefore, because of its connection with the light scattering phenomenon. A good approximation to  $\rho(r)$ , for an *isolated* chain molecule, Eq. (5) below, has been known for some time, and has been used to derive the expression for the light scattering from such a molecule.<sup>1,2</sup> In this paper we will attempt to extend the work to a pair of chain molecules, obtaining in this way an expression for light scattering applicable to polymer solutions at concentrations high enough to be accessible to direct experimental observation.

## II. SEPARATION OF $\rho(r)$ INTO INTERNAL AND EXTERNAL PARTS

A segment in the vicinity of another reference segment may belong either to the same or to a different molecule. Accordingly, the probability of finding a segment, defined above as  $nN\rho(r)d\tau/V$ ,

<sup>1</sup> P. Debye, J. Phys. and Coll. Chem. 51, 18 (1947).

<sup>2</sup> B. Zimm, R. S. Stein, and P. Doty, Polymer Bull. 1, 90 (1945).

\* A preliminary report of these results has already appeared in J. Phys. and Coll. Chem. 52, 260 (1948).

may be divided into two parts, as follows:

$$\frac{nN\rho(r)d\tau}{V} = \left[ \rho_1(r) + \frac{N\rho_2(r)}{V} \right] n d\tau. \quad (2)$$

The first term, the internal part of  $\rho(r)$ , denotes the probability of finding a segment of the same molecule as the reference segment; the second term, the external part, denotes the probability of finding a segment of a different molecule.

The first step in obtaining  $\rho_1(r)$  is to define  $W_{ij}(r)d\tau$  as the probability of finding the  $j$ th segment at distance  $r$  from the  $i$ th segment and in the volume element  $d\tau$ . The theory of random flights<sup>3</sup> gives for this probability the formula:

$$W_{ij}(r)d\tau = \left( \frac{3}{2\pi b^2(|i-j|)} \right)^{\frac{3}{2}} \times \exp\left( \frac{-3r^2}{2b^2(|i-j|)} \right) d\tau, \quad (3)$$

where  $b$  is a constant which depends on the architecture of the chain. By comparison of the definitions, it may be seen that  $\rho_1(r)$  is related to  $W_{ij}(r)$  by the summation:

$$n\rho_1(r) = \frac{2}{n} \sum_{i>j} \sum \left( \frac{3}{2\pi b^2(i-j)} \right)^{\frac{3}{2}} \times \exp\left( \frac{-3r^2}{2b^2(i-j)} \right). \quad (4a)$$

Replacing the summation by integration and substituting the variable  $z=i-j$  leads by simple transformations to the following equation:

$$n\rho_1(r) = 2 \int_0^n \left( \frac{n-z}{n} \right) \left( \frac{3}{2\pi b^2 z} \right)^{\frac{3}{2}} \times \exp\left( \frac{-3r^2}{2b^2 z} \right) dz. \quad (4b)$$

Placing this formula for  $\rho_1(r)$  in Eq. (1) and integrating, the "internal" part of  $I(\vartheta)$  may be obtained.<sup>1,2</sup> The function that is involved will be

called  $P(\vartheta)$  in this paper:

$$P(\vartheta) = \int \rho_1(r) \exp\left( \frac{2\pi i \mathbf{s} \cdot \mathbf{r}}{\lambda} \right) d\tau \\ = \frac{2}{u^2} (e^{-u} - 1 + u), \quad (5)$$

where

$$u = \frac{8\pi^2 b^2 n}{3 \lambda^2} \sin^2 \frac{\vartheta}{2}.$$

### III. THE EXTERNAL PART OF $\rho(r)$

It is now proposed to investigate  $\rho_2(r)$ . We first define a function  $F_2\{(1), (2)\}$  of the coordinates (1) and (2) of the two molecules 1 and 2 such that  $(1/V^2)F_2\{(1), (2)\}d(1)d(2)$  is the probability that these two molecules have the configurations indicated by the particular values of the coordinates (1) and (2) within the range symbolized by  $d(1)$  and  $d(2)$ .

The distribution function of two *particular* segments,  $\mu_1$  from the first molecule and  $\nu_2$  from the second, is obtained by integrating  $(1/V^2)F_2\{(1), (2)\}d(1)d(2)$  over the coordinates of all the other segments of the two molecules, holding the relative coordinates of  $\mu_1$  and  $\nu_2$  fast. The resulting integral will be a function only of  $\mathbf{r}_{\mu\nu}$ , the vector connecting the segments  $\mu_1$  and  $\nu_2$ , if the internal coordinates of  $\mu_1$  and  $\nu_2$  may be ignored.

The probability  $(nN/V)\rho_2(r)d\tau$ , defined above, may now be obtained by summing the integral over all pairs of segments  $\mu_1$  and  $\nu_2$  and multiplying by a numerical factor.

$$\frac{nN\rho_2(r)}{V} = \frac{N}{nV} \sum_1^n \mu_1 \sum_1^n \nu_2 \\ \times \int F_2\{(1), (2)\}d(1)d(2-\mathbf{r}_{\mu\nu}). \quad (6)$$

The symbol  $d(2-\mathbf{r}_{\mu\nu})$  is intended to indicate that the integration, as mentioned above, is to be carried over all coordinates except the relative coordinates of segments  $\mu_1$  and  $\nu_2$ .

In general, the distribution function  $F_2\{(1), (2)\}$  is very complex. It attains a simpler form at infinite dilution, however. In the following para-

<sup>3</sup> See, for example, S. Chandrasekhar, Rev. Mod. Phys. 15, 1 (1943).

<sup>\*\*</sup> The integration is very readily effected in Cartesian coordinates.

graphs we shall work with this limiting form, which will lead to an expression for the light scattering correct to the second power of the concentration. Consideration of the succeeding approximations will be deferred until the final section.

The limit of  $F_2\{(1), (2)\}$  as the concentration is indefinitely decreased will be designated  $F_2^*\{(1), (2)\}$ . The corresponding limit for  $\rho_2(r)$  will be  $\rho_2^*(r)$ .

In a previous paper<sup>4</sup> it was postulated that two thread-like molecules most commonly interact with each other by touching at only one place, so that only one segment from each molecule is involved at one time. If this is so, it is possible to approximate  $F_2^*\{(1), (2)\}$  as a product of the internal distribution functions of the molecules,  $F_1(1)$  and  $F_1(2)$ , and a sum of segment interaction functions,  $\chi(\kappa_1, \lambda_2)$ :

$$F_2^*\{(1), (2)\} = F_1(1)F_1(2) \times \left[1 + \sum_1^n \kappa_1 \sum_1^n \lambda_2 \chi(\kappa_1, \lambda_2)\right]. \quad (7)$$

The functions  $F_1(i)$  are defined as follows:

$\frac{1}{V}F_1(i)d(i)$  is the probability that the molecule  $i$  has the configuration symbolized by  $(i)$  in the hypervolume element  $d(i)$ .

The functions  $\chi(\kappa_1, \lambda_2)$  were discussed in the previous work (4). It is only important here that they are the same for all pairs of segments and that they vanish whenever the distance between the pair of segments involved is much greater than the size of the segments themselves.

We must note that in using this formula configurations in which more than one segment from each molecule are interacting are explicitly ignored. In order for this approximation to be reasonable it is at least necessary that the segments themselves be long and threadlike. Since the segments are arbitrarily chosen, subject only to the restriction that they be much smaller than the whole molecule (and also, as will be seen, much smaller than the wave-length  $\lambda$ ), it is not unduly restrictive that they be long and threadlike.

Eq. (7) may now be introduced into Eq. (6) for  $\rho_2(r)$ . Further, remembering that the func-

tions  $\chi(\kappa_1, \lambda_2)$  are short-range functions while  $F_1(1)$  and  $F_1(2)$  vary relatively slowly with (1) and (2), the integral may be factored to yield the following approximate expression:

$$\begin{aligned} n^2 \rho_2^*(r) = & n^2 + \sum_1^n \mu_1 \sum_1^n \kappa_1 \sum_1^n \lambda_2 \sum_1^n \nu_2 \\ & \times \int \left[ \int F_1(1) d(1 - \mathbf{r}_{\kappa\lambda}) \right] \\ & \times \left[ \int F_1(2) d(1 - \mathbf{r}_{\lambda\nu}) \right] \\ & \times \left[ \int \chi(\mathbf{r}_{\kappa\lambda}) d\mathbf{r}_{\kappa\lambda} \right] d\tau_{\kappa}. \quad (8) \end{aligned}$$

The symbols  $\int \cdots d(1 - \mathbf{r}_{\mu\nu})$  etc., indicate that the integration is to extend over all the coordinates of molecule 1 except the relative coordinates of segments  $\kappa$  and  $\mu_1$ , etc. A more complete discussion of this type of integral has been given on page 177 of reference 4.

It can be seen that  $\int F_1(1) d(1 - \mathbf{r}_{\lambda\mu})$  is the distribution function of the segments  $\kappa_1$  and  $\mu_1$  relative to one another and hence is given by Eq. (3) with  $\kappa$  and  $\mu$  in place of  $i$  and  $j$ , respectively, and  $\mathbf{r}_{\kappa\mu}$  in place of  $\mathbf{r}$ . A similar formula holds for  $\int F_1(2) d(2 - \mathbf{r}_{\lambda\nu})$ . The integral  $\int \chi(\mathbf{r}_{\kappa\lambda}) d\mathbf{r}_{\kappa\lambda}$  has the same value for all pairs of segments  $\kappa$  and  $\lambda$ ; it will be designated by the symbol  $X$  for brevity.

When these results are introduced in (8),  $\rho_2^*(r)$  becomes:

$$\begin{aligned} \rho_2^*(r) = & 1 + \frac{X}{n^2} \left( \frac{3}{2\pi b^2} \right)^3 \\ & \times \sum_{\mu} \sum_{\kappa} \sum_{\lambda} \sum_{\nu} [1/(|\mu - \kappa|)(|\nu - \lambda|)]^{\frac{1}{2}} \\ & \times \int \exp\left(\frac{-3r_{\kappa\mu}^2}{2b^2(|\mu - \kappa|)}\right) \\ & \times \exp\left(\frac{-3r_{\lambda\nu}^2}{2b^2(|\nu - \lambda|)}\right) d\tau_{\kappa}. \quad (9) \end{aligned}$$

In this formula it has been recognized that the coordinates of segment  $\kappa_1$  must be nearly the same as those of segment  $\lambda_2$ , since  $\chi(\kappa_1, \lambda_2)$  vanishes if this is not so. Therefore, the coordinates of  $\kappa_1$  and  $\lambda_2$  have explicitly been made identical.

<sup>4</sup> B. Zimm, J. Chem. Phys. 14, 164 (1946).

It is now convenient to consider the light-scattering problem, which requires the evaluation of the integral:

$$\int \rho_2^*(r) \exp\left(\frac{2\pi i s \cdot r}{\lambda}\right) d\tau. \quad (10)$$

Fortunately, this may be expressed in terms of the function  $P(\vartheta)$  already calculated in Eq. (5).

In any term of the sum in (9),  $r = r_{\kappa\mu} + r_{\kappa\nu}$ , since  $r$  is the vector between the two segments from the different molecules, which in the given term are the segments  $\mu_1$  and  $\nu_2$ . Considering this fact, Eq. (10) may be rewritten:

$$\begin{aligned} & \int \rho_2^*(r) \exp\left(\frac{2\pi i s \cdot r}{\lambda}\right) d\tau \\ &= \int \exp\left(\frac{2\pi i s \cdot r}{\lambda}\right) d\tau + \frac{27X}{(2\pi b^2)^3 n^2} \\ & \times \sum_{\mu} \sum_{\kappa} \sum_{\lambda} \sum_{\nu} \left( \frac{1}{(|\mu - \kappa|)(|\nu - \lambda|)} \right)^{\frac{1}{2}} \\ & \times \left[ \int \exp\left(\frac{-3r_{\kappa\mu}^2}{2b^2(|\mu - \kappa|)} + \frac{2\pi i s \cdot r}{\lambda}\right) d\tau_{\mu} \right] \\ & \times \left[ \int \exp\left(\frac{-3r_{\kappa\nu}^2}{2b^2(|\nu - \lambda|)} + \frac{2\pi i s \cdot r_{\kappa\nu}}{\lambda}\right) d\tau_{\nu} \right]. \quad (11) \end{aligned}$$

The first term of (11) may be neglected except for very small angles of scattering when  $s$  is also very small. The second part of the expression may be factored into two factors, each of which is similar to Eq. (5).

$$\begin{aligned} & \int \rho_2^*(r) \exp\left(\frac{2\pi i s \cdot r}{\lambda}\right) d\tau \\ &= X \left\{ \frac{1}{n} \left( \frac{3}{2\pi b^2} \right)^{\frac{1}{2}} \sum_{\kappa} \sum_{\mu} \frac{1}{(|\mu - \kappa|)^{\frac{1}{2}}} \right. \\ & \times \int \exp\left(\frac{-3r^2}{2b^2(|\mu - \kappa|)} + \frac{2\pi i s \cdot r}{\lambda}\right) d\tau \left. \right\} \\ & \times \left\{ \frac{1}{n} \left( \frac{3}{2\pi b^2} \right)^{\frac{1}{2}} \sum_{\lambda} \sum_{\nu} \frac{1}{(|\nu - \lambda|)^{\frac{1}{2}}} \right. \\ & \times \int \exp\left(\frac{-3r^2}{2b^2(|\nu - \lambda|)} + \frac{2\pi i s \cdot r}{\lambda}\right) d\tau \left. \right\} \\ &= n^2 X P^2(\vartheta). \quad (12) \end{aligned}$$

Finally, the use of (12) and (5) in (1) gives the expression for the intensity of the light scattered by a unit volume of solution as

$$I(\vartheta) = \frac{kn^2 N}{V} \left[ P(\vartheta) + \frac{Nn^2 X}{V} P^2(\vartheta) \right]. \quad (13a)$$

If conversion is made to the usual concentration units, weight per unit volume, so that  $c = NM/VN_0$ , where  $M$  is the molecular weight of the chain molecule, (13b) is obtained,

$$I(\vartheta) = Kc [MP(\vartheta) - 2A_2 M^2 P^2(\vartheta)c], \quad (13b)$$

where  $A_2 = -N_0 n^2 X / 2M^2$ , with  $N_0$  Avogadro's number, and  $K = n^2 k / M^2$ .

Comparison with Eq. (7) shows that

$$\begin{aligned} A_2 = -\frac{N_0}{2M^2 V} \int [F_2\{(1), (2)\} \\ - F_1(1)F_1(2)] d(1)d(2). \quad (14) \end{aligned}$$

It is already known,<sup>4,5</sup> however, that if the osmotic pressure  $\Pi$  of the solution is represented as a power series in the concentration,  $A_2$  is the coefficient of the second power.

$$\Pi = RT[(c/M) + A_2 c^2 + A_3 c^3 + \dots]. \quad (15)$$

Analogously, the first terms of the expression for the reciprocal of the intensity of the scattered light, multiplied by  $c$ , are:

$$[Kc/I(\vartheta)] = [1/MP(\vartheta)] + 2A_2 c. \quad (16)$$

It will be shown later that expression (16) is a good approximation to the true state of affairs at much higher concentrations than its reciprocal, expression (13b). When  $\vartheta$  is zero,  $P(\vartheta)$  is unity, and (16) is seen to be the derivative of the osmotic pressure over  $RT$  with respect to  $c$ , in agreement with the well-known results from fluctuation theory.<sup>6</sup>

The simplicity of this result is noteworthy. The intercept of the plot of  $[Kc/I(\vartheta)]$  vs.  $c$  depends on  $\vartheta$ , but the initial slope does not.

The approximation which is most likely to have a serious effect on this result is that the

<sup>4</sup> W. G. McMillan and J. E. Mayer, J. Chem. Phys. **13**, 276 (1945).

<sup>5</sup> S. Bhagavantam, *The Scattering of Light and Raman Effect* (Chemical Publishing Company, Brooklyn, New York, 1942).

thread-like molecules exert forces on each other through only one segment of each molecule at a time. This may fail especially for very long and highly coiled threads. It remains for experiment or more involved calculations to assess the magnitude of the deviations.

As a corollary to the linear relation (16), it may be remarked that the reciprocal of the quantity which has been called the dissymmetry coefficient,  $q$ , should be likewise linear. If  $\vartheta_1$  and  $\vartheta_2$  are two angles equidistant from the normal to the direction of the incident beam,  $q = [I(\vartheta_1)/I(\vartheta_2)] - 1$ ,  $\vartheta_2$  being the greater angle. Use of (16) results in the relation

$$\frac{1}{q} = \frac{1}{[q]} + \frac{2A_2MP(\vartheta_1)}{[q]}c, \quad (17)$$

where  $[q]$  is the limit  $q$  approaches as  $c$  approaches zero. Such a linearity has already been observed empirically.<sup>7</sup>

It may be noted that there is nothing in the derivation which restricts the procedure to a coiling chain. If, for instance, the chain were rigid, in the shape of a straight line, the same formulae would hold, provided only that  $P(\vartheta)$  is given by:

$$P(\vartheta) = \frac{1}{x} \int_0^{2x} \frac{\sin u}{u} du - \left( \frac{\sin x}{x} \right)^2, \quad (18a)$$

$$x = \frac{2\pi L \sin(\vartheta/2)}{\lambda}. \quad (18b)$$

$L$  is the end-to-end length of the chain and  $u$  is a variable of integration. The function

$$\int_0^y (\sin u/u) du$$

is the so-called "integral sine," which may be found in tables of functions.

#### IV. CONCERNING HIGHER POWERS OF THE CONCENTRATION

In the preceding section the limiting distribution function,  $F_2^*\{(1), (2)\}$ , was used to obtain

an expression for the light scattering valid to the term in the second power of the concentration. In this section a short examination will be made of the nature of some of the higher terms.

The deviations of  $F_2\{(1), (2)\}$  from its limiting form at infinite dilution,  $F_2^*\{(1), (2)\}$ , may be expressed in terms of interactions of the molecules 1 and 2 with other molecules in their neighborhood. Adapting the results of Mayer and Montroll<sup>8</sup> we assume that  $F_2\{(1), (2)\}$  is given by the equation,

$$F_2\{(1), (2)\} = F_2^*\{(1), (2)\} \\ \times \{1 + \sum_{m \geq 1} H_{2m}\{(1), (2)\} v^{-m}\}, \quad (19)$$

when  $v$  is  $V/N$ , the volume per molecule, and the  $H_{2m}\{(1), (2)\}$  are complicated functions of the coordinates of molecules 1 and 2, as discussed below.

The interaction of two molecules,  $i$  and  $j$ , at infinite dilution may be conveniently described by a function  $g_2^*\{i, j\}$ ,

$$g_2^*\{(i), (j)\} = F_2^*\{(i), (j)\} - F_1(i)F_1(j). \quad (20)$$

The first coefficient in the sum in (19),  $H_{21}\{(1), (2)\}$ , will now be given by:

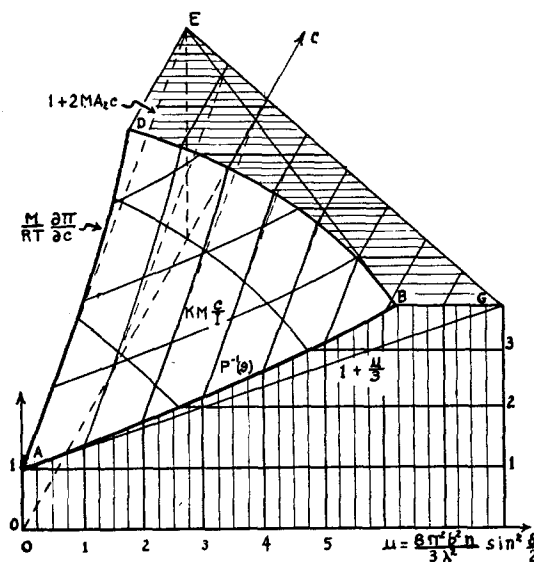


FIG. 1. The reciprocal intensity surface,  $KMc/I$ .

<sup>7</sup> P. Doty, W. Affens, and B. Zimm, *Trans. Faraday Soc.* **42B**, 66 (1946).

<sup>8</sup> J. E. Mayer and E. Montroll, J. Chem. Phys. 9, 2 (1941), Eqs. (40), (44), and (52).

$$H_{21}\{(1), (2)\} = \int g^*\{(1), (3)\} g^*\{(2), (3)\} d(3) \\ + \int g^*\{(1), (2)\} g^*\{(1), (3)\} \\ \times g^*\{(2), (3)\} d(3). \quad (21)$$

Considering for the moment the first integral in (21), comparison with the preceding section shows that we must evaluate the expression:

$$\sum_1^n \mu_1 \sum_1^n \nu_2 \int \exp(2\pi i \mathbf{s} \cdot \mathbf{r}/\lambda) \\ \times g^*\{(1), (3)\} g^*\{(2), (3)\} d(1)d(2)d(3). \quad (22)$$

If the position of one of the segments,  $\xi_3$ , of 3 is chosen as origin of coordinates, and  $\mathbf{s} \cdot \mathbf{r}_{\mu\nu} = \mathbf{s} \cdot \mathbf{r}_{\mu\xi} + \mathbf{s} \cdot \mathbf{r}_{\xi\nu}$ , then (22) divides into two factors, one containing the integration over  $d(1)$  and the other over  $d(2)$ , in a form somewhat similar to Eq. (12). The final result is to introduce a term  $4A_2^2 P^4(\vartheta) c^2$  into Eq. (13b).

The second integral in (21) resists this method of attack, at least if applied rigorously. In recognition of this irreducibility, it has been used to define<sup>4,5</sup> a quantity,  $A_3$ , which has already appeared in Eq. (15),

$$A_3 = -\frac{N_0^2}{3M^3V} \int g^*\{(1), (2)\} g^*\{(2), (3)\} \\ \times g^*\{(1), (3)\} d(1)d(2)d(3). \quad (23)$$

For the light scattering problem, we must now define a new function,  $Q(\vartheta)$ , by the equation:

$$Q(\vartheta)A_3 = -\frac{N_0^2}{3n^2M^3V} \left\{ \sum \mu_1 \sum \nu_2 \right. \\ \times \int g^*\{(1), (2)\} g^*\{(2), (3)\} g^*\{(1), (3)\} \\ \left. \times \exp(2\pi i \mathbf{s} \cdot \mathbf{r}_{\mu\nu}/\lambda) d(1)d(2)d(3) \right\}. \quad (24)$$

Since  $s = 2 \sin(\vartheta/2)$  approaches zero as  $\vartheta$  approaches zero,  $Q(0) = 1$ . The real part of  $\exp(2\pi i \mathbf{s} \cdot \mathbf{r}_{\mu\nu}/\lambda)$  is equal or less than unity for all other values of  $\vartheta$ , so that  $Q(\vartheta)$  must also be less than unity for finite values of  $\vartheta$ .

The next higher term in the power series for the light scattering results from  $H_{22}\{(1), (2)\}$ . An analysis similar to the preceding shows that it can be expressed in terms of  $A_2$  and  $A_3$  with

$P(\vartheta)$  and  $Q(\vartheta)$ , plus  $A_4$  in association with a new function of  $\vartheta$ . It seems profitless, in the present development, to follow the investigation further along this line.

We will now use the preceding results to write an expression for  $I(\vartheta)$ , correct to the third power of the concentration,

$$I(\vartheta, c) = K \{ MP(\vartheta)c - 2A_2M^2P^2(\vartheta)c^2 \\ + [4A_2^2M_2^3P^4(\vartheta) \\ + 3A_3M_2^2P^2(\vartheta)Q(\vartheta)]c^3 + \dots \}. \quad (25)$$

Taking the reciprocal of (25) leads to the form which converges more rapidly:

$$K \frac{c}{I(\vartheta, c)} = \frac{1}{MP(\vartheta)} + 2A_2c \\ + [3A_3Q(\vartheta) - 4A_2^2P(\vartheta)(1 - P(\vartheta))]c^2 + \dots \quad (26)$$

The right-hand side of Eq. (26) is correct to the second power of  $c$ . The coefficients  $A_2$  and  $A_3$  are the same as those appearing in Eq. (15) for the osmotic pressure. The function  $Q(\vartheta)$  has not yet been calculated in detail. Since  $P(\vartheta)$  and  $Q(\vartheta)$  both approach unity as  $\vartheta$  approaches zero, the right-hand side of Eq. (26) approaches the derivative of Eq. (15) with respect to  $c$  as  $I$  approaches zero.

## V. GRAPHICAL REPRESENTATION OF THE RECIPROCAL INTENSITY FUNCTION

The reciprocal intensity function,  $Kc/I$ , depends on the two independent variables of concentration,  $c$ , and angle,  $\vartheta$ . It may be represented by a surface in three-dimensional space, putting  $MKc/I$  along the vertical axis and  $c$  and  $\vartheta$  along the horizontal axes. Such a surface is shown in Fig. 1 for the scattering from a coiling chain solute.

The surface, which is somewhat concave, is represented by  $ABD$  in the figure. In general, it is tangent at  $A$  to the plane  $AGE$ , whose boundary  $AG$  at the  $c=0$  plane is the limiting tangent of  $P^{-1}(\vartheta)$ , which is  $1+u/3$ , and whose boundary  $AE$  at the plane  $\vartheta=0$  is the limiting tangent  $1+2MA_2c$ . The result peculiar to this study, that  $A_2$  is independent of  $\vartheta$ , is represented by the fact that the reciprocal intensity surface is tangent along  $AB$  to the *cylindrical* surface

$ABE$ , all of whose elements are parallel to the  $\vartheta = 0$  plane and have the slope  $2MA_2$ .

Experimental points will generally lie in the interior parts of the surface, while the quantities of interest, molecular length and extension, are

only obtainable from the boundary at  $c = 0$ . A process of extrapolation is therefore necessary. Knowledge of the linearity of the surface at small values of  $c$  is important in performing the extrapolation properly.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 16, NUMBER 12 DECEMBER, 1948

## Apparatus and Methods for Measurement and Interpretation of the Angular Variation of Light Scattering; Preliminary Results on Polystyrene Solutions

BRUNO H. ZIMM

*Department of Chemistry, University of California, Berkeley 4, California*

(Received June 2, 1948)

A photoelectric apparatus for the measurement of the angular dependence of light scattering from solutions is described in detail and its performance is discussed. Methods of calculation for the determination of the average extension of the scattering molecules from the data are described. Data are presented for two fractions of polystyrene in various solvents, showing the effect of changing solvent power and temperature, and also confirming a theoretically derived formula for the concentration dependence of the scattering.

### I. INTRODUCTION

WHEN light is scattered from a macromolecule, such as a high polymer chain, an intensity distribution results which may be considered as a simple form of interference pattern. From appropriate measurements on the pattern the spatial extension of the molecule may be deduced.

The present paper describes new apparatus for obtaining the intensity distribution of the scattering. Several previous investigators<sup>1,2,3</sup> have also described apparatus for this purpose. The present equipment incorporates some important refinements over the previous types.

Theoretical developments, such as described by Debye<sup>4</sup> and by the author in the preceding paper,<sup>5</sup> are indispensable to the proper interpretation of the raw data. A method of application of the theory is therefore presented in some detail.

Finally, data on polystyrene solutions are

given. They seem to confirm the formulae derived in the preceding paper,<sup>5</sup> in addition to having physico-chemical interest of their own.

Although the average spatial extension of the molecules of a polymeric material affects most of its properties, light scattering from dilute solution seems to be the only way this dimension can be unambiguously determined. Approximate relative values can be found in some cases from viscosity measurements. For example, it has long been recognized that the "intrinsic viscosity" of a given polymer is smaller in thermodynamically poor solvents than in good ones, and this effect has been interpreted as indicating a curling up and contraction of the polymer chain in the unfavorable solvent.

An attempt has already been made to compare viscosity and light-scattering measurements of the solvent effect in polystyrene solutions.<sup>6</sup> The results were confusing in that a large change occurred in the viscosity but very little in the light scattering. The measurements have been repeated in part with the new apparatus and the earlier data have been found to be in error by a small but significant amount. In the new meas-

<sup>1</sup> R. S. Stein and P. M. Doty, *J. Am. Chem. Soc.* **68**, 159 (1946).

<sup>2</sup> P. P. Debye, *J. App. Phys.* **17**, 392 (1946).

<sup>3</sup> R. Speiser and B. A. Brice, *J. Opt. Soc. Am.* **36**, 364 (1946).

<sup>4</sup> P. Debye, *J. Phys. Coll. Chem.* **51**, 18 (1947).

<sup>5</sup> B. Zimm, *J. Chem. Phys.* **16**, 1093.

<sup>6</sup> P. Doty, W. Affens, and B. Zimm, *Trans. Faraday Soc.* **42B**, 66 (1946).