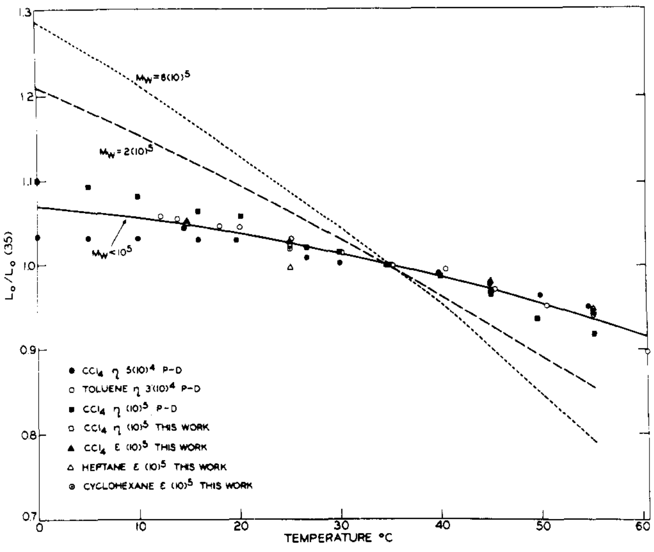

Figure 2. $L_0/L_0(35°)$ as a function of temperature.

ternatives of L_0 independent of temperature and L_0 variation with temperature as shown in Figure 2. From the values of ϵ_0 and ϵ_∞ we determined the average molecular dipole moment at each temperature (for carbon tetrachloride and for n-heptane separately) and attempted to determine the slope of a dipole moment vs. temperature plot. The expected change in dipole moment is small and the errors in the dipole moment determination are sufficiently large (due to the deliberate use of low concentrations) so that either hypothesis is consistent with the data. The dielectric relaxation time is a more sensitive probe of L_0 varying nearly as L_0^3 whereas the dipole moment is linear in L_0.

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Light Scattering from Correlated Polymer Systems

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ABSTRACT: The use of irreducible representation coefficients for angular dependent correlations is proposed for light scattering from correlated polymer systems, which have long range orientational correlations. A set of rather general equations for this scattering is derived, using these irreducible representations. The general angular dependence of the scattering of plane polarized light is found, and analytic forms for the characteristic patterns of the V_v and H_v patterns are given. Furthermore, it is shown that the irreducible representations give rather remarkably simple equations for the molecular factor in the scattering cross section. Explicit expressions for thin, oriented rods are given.

The theory of light scattering of molecular systems in which the correlation length is short compared to the wavelength of the light is quite well understood. However, in systems in which the correlation length is long, such as polymeric materials, there is still some room for theoretical developments. There are effects, due to the persistence of long range correlations, which cannot be accounted for by simple theories.

In polymer materials, the studies of Stein and his school[1] reveal that the depolarized component has a peculiar angular dependence. The intensity pattern under crossed polarizers has a characteristic four-leaved clover shape, with axes at $\pi/4$ from the axes of the polarizers. The application of the standard theory leads to a maze of complicated integrals, and therefore, the approach has been to formulate a physically simple and reasonable model and then carry out the integrals of the standard theory.[2] This approach is quite successful when the scattering is intramolecular, and the correlation between the molecules is unimportant. A typical example is a spherulitic polymer material.

In fibrous materials, this simple approach cannot be carried to its end, due to the very difficult integrations, in the first place, and to the fact that the interfiber angular correlations cannot be ignored. The problem of the angular correlations is in itself a nontrivial one, and fitting the observations to a specific model may be a scientifically unattractive proposition.

The purpose of the present communication is twofold: first we use a general technique, Racah algebra, to find the angular dependence for the polarized light scattered from an arbitrary but isotropic system; second, we use irreducible correlation function expansions for the angular correlations. This produces some remarkable simplifications in the otherwise very complex equations.

In summary, the theoretical formulation is general and no specific model has to be formulated to interpret the angular dependence of the polarized light. The particular trick of using Racah algebra was first proposed by Ben-Reuven and Gershon,[3] in a study of dynamical effects in inelastic light scattering from molecular fluids. To treat the light scattering part, we will use an extension and generalization of this work,[4] which includes circularly polarized light, and also helical correlations. This formalism, which is based on the polar form of the coherency matrix, permits a very symmetric treatment of the light scattering. As in the work of Ben-Reuven and Gershon, we find that the scattering cross sections are products of photon, or external geometry invariants, which depend on the incident and scattered polarizations, and the scattered angles and molecular invariants, which depend on the nature of the systems.

We show that if the irreducible rather than the invariant expansions[5,6] are used, then, much simpler and physically meaningful formulas can be obtained. The irreducible representations are classified by their chirality or heliticity x. Fully polarized radiation scattering, like the X-ray or neutron scattering,[7] can give information only about the most symmetric representation, the cylindrically symmetric, or $x = 0$ irreducible coefficients. Therefore, the structure of the molecular fluid cannot be determined from X-ray or neutron scattering experiment alone. In the case of light scattering, the situation is more favorable since polarization analysis can yield information about some coefficients in the irreducible representations with $x = 0, \pm 1, \pm 2$.

In section I we give a summary of molecular correlation expansions and in section II the polar form of the coherency matrix is briefly explained. In section III, we use these elements to reformulate a general light scattering equation, which is the sum of the products of the photon and molecular invariants. The photon invariants are explicitly evaluated in section IV. It is found that for very long ranged correlations and small angles, the typical patterns of the depolarized H_v scattering are obtained, but also that there is no obvious relation to the structure of the material. The molecular invariants are discussed in section V, where we get the irreducible coefficients in a very direct way. The case of long, thin rods is given as an example.

I. Invariant and Irreducible Expansions

We assume that the system is formed by polymer molecules, and that each molecule is formed by bonds which can be represented by a definite polarizability tensor, $\hat{\epsilon}$, such that the induced dipole moment, $\mathbf{m}(i)$, is

$$\mathbf{m}(i) = \hat{\boldsymbol{\epsilon}}(i) \cdot \mathbf{E}_0 \tag{1}$$

where $\mathbf{E_0}$ is the local field at the point $\mathbf{R_i}$, where the bond unit i is located. Any realistic treatment of polymers gets the polarizability by performing the ensemble average of the chain system using models with angle dependent potentials.[8] These models are rather involved, and still present unsolved problems in their mathematics. It is therefore only a reasonable approach to make model polymers by assuming that they are made up of units, which may even be several monomers long. These building blocks have a rather constant or smoothly varying orientation within the polymer chain. The polarizability tensor can be written in polar form[9]

$$\epsilon_0^0(0) = (^1/_3)^{1/2}(\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}) \tag{2}$$

$$\epsilon_0^0(0) = (^1/_6)^{1/2}(2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy}) \tag{3}$$

$$\epsilon_{\pm 2}^2(0) = (^1/_2)(\epsilon_{xx} - \epsilon_{yy}) \tag{4}$$

where ϵ_{xx}, ϵ_{yy}, and ϵ_{zz} are the Cartesian components of the polarizability tensor. The polar components defined by the above equations have the following physical interpretation: ϵ_0^0 is the average polarizability, ϵ_0^2 and ϵ_2^2 are the deviations from spherical symmetry of the polarizability. For cylinders, $\epsilon_{\pm 2}^2 = 0$ and the polarizability tensor is a two-axis ellipsoid. In the most general case ϵ is a three-axis ellipsoid.

When the scattering unit is rotated through the euler angles $\Omega \equiv \alpha, \beta, \gamma$ then the polarizability tensor transforms according to

$$\epsilon_\mu^2(\Omega) = \sum_{\mu' = -2}^{2} D_{\mu\mu'}^2(\Omega)\epsilon_{\mu'}^2 \tag{5}$$

where $D_{\mu\mu'}^m(\Omega)$ is the generalized spherical harmonic of Wigner, which is also the irreducible representation of the rotation operator in O_3.

In a system of polymer molecules, the scattering intensity is due to the interference of scattered electric fields from two different scattering units. These units, which are much smaller than the wavelength of the light, can belong to the same polymer molecule ("self" scattering) or to different molecules ("distinct" scattering). In any case, the result will depend on the two polarizability tensors, say $\epsilon(\Omega_1)$ and $\epsilon(\Omega_2)$, of the units 1 and 2. If the orientational correlations persist for a sufficiently long range, then the scattering will depend on the relative orientations of scattering units 1 and 2. In an arbitrary reference frame, we will need a total of eight angles and one distance to define the geometry completely, namely three euler angles Ω_1, for scatterer 1, three for scatterer 2, and two more angles θ_{12}, $\zeta_{12} \equiv \hat{\mathbf{R}}_{12}$ which define the orientation of the distance between 1 and 2, the vector $\mathbf{R}_{12}$.

For isotropic systems, the rotational invariance requires that the correlations are independent of the reference frame used to define the eight angles. Therefore, there will be only five truly independent angles. The polarizability tensors, being already rather symmetric, will have only a few ways of orienting relative to each other. If we neglect helical correlations (optically inactive systems) 12 linearly independent orientations can exist. If the scattering unit is cylindrically symmetric, then only three types of correlations exist in optically inactive systems, and five in optically active ones.

Let us explain this point in a little more detail. The correlation function for a pair of molecules $g(\mathbf{X}_1,\mathbf{X}_2)$ where $\mathbf{X}_i = \mathbf{R}_i$, Ω_i *can be expanded as*[5]

$$g(\mathbf{X}_1, \mathbf{X}_2) = \sum_{\substack{mnl \\ \mu\nu}} \hat{g}_{\mu\nu}^{mnl}(R_{12})\hat{\Phi}_{\mu\nu}^{mnl}(\boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2, \hat{\mathbf{R}}_{12}) \tag{6}$$

with

$$\hat{\Phi}_{\mu\nu}^{mnl}(\Omega_1, \boldsymbol{\Omega}_2, \hat{\mathbf{R}}_{12}) = [(2m + 1)(2n + 1)]^{1/2} \times \sum_{\mu'\gamma'\lambda'} \begin{pmatrix} m & n & l \\ \mu' & \nu' & \lambda' \end{pmatrix} D_{\mu\mu'}^m(\boldsymbol{\Omega}_1)D_{\nu\nu'}^n(\boldsymbol{\Omega}_2)D_{0\lambda'}^l(\hat{\mathbf{R}}_{12}) \tag{7}$$

where we have used the standard notation for Wigner's $3 - J$ symbols. The coefficients $\hat{g}_{\mu\nu}^{mnl}(\mathbf{R}_{12})$ depend only on the distance between the stterers.

The expression $\hat{\Phi}_{\mu\nu}^{mnl}$ is invariant under rigid rotation of the reference frame and can always be expressed as a linear combination of scalar products or contractions of vector and tensor quantities. In our case m,μ (and n,ν) can only take the values $m = 0, 2$ and $\mu = 0, \pm 2$ and for cylindrical symmetry[5] $\mu = 0$; therefore, the only relevant coefficients are, in this case

$$\hat{g}_{00}^{220}; \quad \hat{g}_{00}^{222}; \quad \hat{g}_{00}^{224} \tag{8}$$

If helical correlations are possible we also have

$$\hat{g}_{00}^{221}; \quad \hat{g}_{00}^{223} \tag{9}$$

different from zero.

It has been shown[6] that rather drastic simplifications occur when instead of using the invariant expansion (eq 6) we use the irreducible expansion. The coefficients of the irreducible and invariant expansions are related by a simple orthogonal transformation. Since the reference frame is arbitrary we may allign the vector $\mathbf{R}_{12}$ with the z axis. Therefore the angle $\hat{\mathbf{R}}_{12} = 0$ and, using the property of the generalized spherical harmonics,[9]

$$D^l_{0\lambda'}(0) = \begin{cases} 0 & \text{if } \lambda' \neq 0 \\ 1 & \text{if } \lambda' = 0 \end{cases}$$

we get for (6)

$$g(\mathbf{X}_1, \mathbf{X}_2) = \sum_{\substack{mnl \\ \mu\nu}} \hat{g}^{mnl}_{\mu\nu}(\mathbf{R}_{12})[(2m + 1)(2n + 1)]^{1/2} \times \sum_x \begin{pmatrix} m & n & l \\ x & -x & 0 \end{pmatrix} D^m_{\mu x}(\mathbf{\Omega}_1) D^n_{\nu -x}(\mathbf{\Omega}_2) \quad (10)$$

which can be rearranged by exchanging the x and l sums

$$g(\mathbf{X}_1, \mathbf{X}_2) = \sum_{\substack{mn \\ \mu\nu, x}} g^{mn}_{\mu\nu, x}(\mathrm{R}_{12}) \Phi^{mn}_{\mu\nu, x} \quad (11)$$

with

$$\Phi^{mn}_{\mu\nu, x} = [(2m + 1)(2n + 1)]^{1/2} D^m_{\mu x}(\mathbf{\Omega}_1) D^n_{\nu -x}(\mathbf{\Omega}_2) \quad (12)$$

and

$$g^{mn}_{\mu\nu, x}(\mathbf{R}_{12}) = \sum_l \begin{pmatrix} m & n & l \\ x & -x & 0 \end{pmatrix} \hat{g}^{mnl}_{\mu\nu}(\mathbf{R}_{12}) \quad (13)$$

The transformation (eq 13) is orthogonal and the inverse can be obtained quite simply from

$$\hat{g}^{mnl}_{\mu\nu}(\mathbf{R}_{12}) = (2l + 1) \sum_x \begin{pmatrix} m & n & l \\ x & -x & 0 \end{pmatrix} g^{mn}_{\mu\nu, x}(\mathbf{R}_{12}) \quad (14)$$

The expansion (eq 11) has a physical interpretation, which becomes simple for cylinders ($\mu = \nu = 0$). First notice that the index x corresponds to the chirality, or helicity, of the corresponding irreducible representation. The irreducible representations do not mix, in the sense that most physical properties can be expressed as sums over x, with no cross-terms. Again, to keep matters simple, let us write the angular functions for cylinders (we drop $\mu = \nu = 0$ from the symbols for simplicity)

$x = 0$

$$\Phi^{22}_0 = {}^5/_4(3 \cos^2 \beta_1 - 1)(3 \cos^2 \beta_2 - 1) \quad (15)$$

$x = \pm 1$

$$\Phi^{22}_{\pm 1} = -\frac{15}{2} \sin \beta_1 \cos \beta_1 \sin \beta_2 \cos \beta_2 e^{\pm i(\alpha_1 - \alpha_2)} \quad (16)$$

$x = \pm 2$

$$\Phi^{22}_{\pm 2} = \frac{15}{8} \sin^2 \beta_1 \sin^2 \beta_2 e^{\pm 2(\alpha_1 - \alpha_2)i} \quad (17)$$

clearly the coefficient g^{22}_0 corresponds to arrangements of the polarizability tensor which are cylindrically symmetric around the interunit axis, just like a σ molecular orbital in a diatomic molecule. In the configurations represented by $x = \pm 1$, one of the tensors is rotated with respect to the other, but only one node in either the real or imaginary parts exists as $\alpha_1 - \alpha_2$ is varied from 0 to 2π. This is the analog to the π molecular orbital, but with the addition that the sign of x, which is that of $\alpha_1 - \alpha_2$, can be interpreted as the sense of the rotation. If the weight of the right-handed rotations is equal to that of the left-handed ones, then $g^{22}_x = g^{22}_{-x}$ and the system will exhibit no preferred helicity or possible optical activity. For $x = \pm 2$ the discussion is similar, and the geometry is that of the δ molecular orbital.

We can see from (14) that for systems of no preferred helicity, $\hat{g}^{221}(\mathbf{R}_{12})$ and $\hat{g}^{223}(\mathbf{R}_{12})$ must be identically zero.

II. Coherency Matrices

Let us summarize here some definitions of previous work.[4] For arbitrarily polarized light, it is convenient to use the polar form of the coherency matrix,[4] which transforms like a true tensor. These quantities are very simply related to the Stokes parameters,[11] which characterize the polarization state of the light.

Let us summarize first some of the main properties. The state of polarization of light is given by the coherency matrix

$$\mathbf{J} = \begin{bmatrix} J_{11} & J_{12} \\ J_{21} & J_{22} \end{bmatrix} \quad (18)$$

where

$$J_{\alpha\beta} = \overline{E_\alpha E^*_\beta} \quad (19)$$

$$\alpha, \beta = 1, 2$$

where the bar indicates time average and E_α is the amplitude of the electric field in the direction α, and is written in complex form

$$E_\alpha = E^0_\alpha e^{i[\mathbf{k}\cdot\mathbf{r} - \omega t + \delta]} \quad (20)$$

with E^0_α the maximum amplitude of the oscillation, $\mathbf{k}$ the wave vector, $\mathbf{r}$ the position at which the field E_α is measured, ω the angular frequency, t the time, and δ the initial phase. The directions 1, 2 are always mutually perpendicular, and perpendicular to $\mathbf{k}$. We always take $\mathbf{k}$ as the z axis, and the directions 1 and 2 as the x and y axes.

Let us now convert (18) to the polar form

$$K^0_0 = \frac{1}{\sqrt{3}}(J_{11} + J_{22}) \quad (21)$$

$$K^1_0 = (i/\sqrt{2})(J_{12} - J_{21}) \quad (22)$$

$$K^2_0 = -(1/\sqrt{6})(J_{11} + J_{22}) \quad (23)$$

$$K^2_{\pm 2} = ({}^1/_2)(J_{11} - J_{22} \pm i(J_{12} + J_{21})) \quad (24)$$

The numbers K^m_μ are very closely related to the Stokes parameters, and the properties of the light can be easily interpreted in terms of them.

The total intensity is

$$I_{\text{tot}} = (1/\sqrt{3})[2K^0_0 - \sqrt{2}K^2_0] \quad (25)$$

$$I_{\text{pol}} = [4K^2_2 K^2_{-2} + 2(K^1_0)^2]^{1/2} \quad (26)$$

Plane polarized light of intensity I at an angle ζ with the $x \equiv (1)$ direction is represented by

$$K^0_0 = (1/\sqrt{3})I; \quad K^2_0 = (-1/\sqrt{6})I; \quad K^2_{\pm 2} = (I/2)e^{\pm 2i\zeta}; \quad K^1_0 = 0 \quad (27)$$

while circularly polarized light is represented by

$$K^0_0 = (1/\sqrt{3})I; \; K^2_0 = (-1/\sqrt{6})I; \; K^2_{\pm 2} = 0; \quad K^1_0 = \pm I/\sqrt{2} \quad (28)$$

where the sign of K^l_0 indicates left or right polarization.

The polar form of the coherency matrix transforms like a true tensor under a rotation through an angle Υ[9]

$$K^m_\mu(\Upsilon) = \sum_{\mu'} K^m_{\mu'}(0) D^m_{\mu\mu'}(\Upsilon) \quad (29)$$

Away from the radiating center, the longitudinal components vanish.

The intensity at a certain angle can be computed from $\mathbf{K}$ by solving the relations in eq 21–24. The result is

$$I_{11} = \sum_{m,\mu} A^m_\mu K^m_\mu \quad (30)$$

with coefficients, for linearly polarized light

$$A_0^0 = 1/\sqrt{3};\, A_0^2 = -1/\sqrt{6};\, A_{\pm 2}^2 = {}^1/_2 \qquad (31)$$

The desired scattering equation should relate the coherency matrix of the incoming light to the coherency matrix of the outgoing light, by a linear relation of the form

$$K_\sigma^s(f) = \sum_{t,\tau} \mathbf{S}_{\sigma\tau}^{st} K_\tau^t(i) \qquad (32)$$

Equation 32 is completely general, since any type of incoming and scattered light is included in it. Sometimes, however, one wants to get a more direct relation between the measured intensities. It is quite straightforward to see that, if the incident light intensity is given by (27), and the scattered intensity is measured in an arbitrary direction given by the eulerian angles $\Upsilon = \zeta,\theta,\psi$ it is given by

$$I^f = \mathbf{S}(\Upsilon) I^i \qquad (33)$$

$$\mathbf{S}(\Upsilon) = \sum_{st\sigma\tau} A_\sigma^s(f) \mathbf{S}_{\sigma\tau}^{st}(\Upsilon) \hat{K}_\tau^t(i) \qquad (34)$$

where I^i is the incoming intensity, and $\hat{K}_\tau^t(i)$ are the coefficients of the coherency matrix for the incident light. The suffix (f) denotes the corresponding quantities for the scattered light.

III. Light Scattering Formalism

The arguments presented in this section are group theoretical, and therefore apply to both equilibrium and time dependent light scattering. But since we want to discuss equilibrium scattering, our explicit expressions will be the equilibrium ones.

In Cartesian form the coherency matrix of the scattered light is[3-5,11]

$$I_{\alpha\beta}^f = A \sum_{a,b}^{V} \langle \mathbf{E}_\alpha(a) \mathbf{E}_\beta^*(b) \exp(i\mathbf{K}\cdot\mathbf{R}_{ab})\rangle \qquad (35)$$

with

$$A = k_i^4/(16\pi^2 R_0{}^2) \qquad (36)$$

here k_i is the incident wave vector, R_0 is the distance to the sample, $\mathbf{E}_\alpha(a)$ is the electric field amplitude (eq 20) scattered by unit (bond, molecule, monomer) a, located at $\mathbf{R}_a$. It is proportional to the induced dipole moment $\mathbf{m}(a)$, given by eq 1. Also

$$\mathbf{K} = \mathbf{k}_i - \mathbf{k}_f \qquad (37)$$

$$\mathbf{R}_{ab} = \mathbf{R}_a - \mathbf{R}_b \qquad (38)$$

and the brackets $\langle\rangle$ indicate esemble average. Calling $\mathbf{n}_1^i$, $\mathbf{n}_2^i$ the unit vectors in the x,y directions of the incident light frame, and $\mathbf{n}_1^f$, $\mathbf{n}_2^f$ the corresponding quantities for the scattered beam, and also, using the Rayleigh expansion[9]

$$e^{i\mathbf{K}\cdot\mathbf{R}_{ab}} = \sum_{l=0}^{\infty} i^l(2l+1) j_l(K\mathbf{R}_{ab}) \mathbf{C}^l(\hat{\mathbf{K}})\cdot\mathbf{C}^l(\hat{\mathbf{R}}_{ab}) \qquad (39)$$

where the tensor $\mathbf{C}^l(\hat{\mathbf{K}})$ has components $C_\lambda^l(\hat{\mathbf{K}})$ which are Racah's spherical harmonics (in Edmonds phase convention[9]), and we have used the scalar product symbol for tensors, defined by

$$\mathbf{A}^l\cdot\mathbf{B}^l = \sum_{\lambda=-l}^{l} (-1^\lambda A_\lambda^l B_\lambda^l) \qquad (40)$$

Furthermore, define the tensors

$$(\mathbf{W}_{\alpha\gamma})_\mu^m = [\mathbf{n}_\alpha^0 \times \mathbf{n}_\gamma^f]_\mu^m \qquad (41)$$

where we have used the direct or Kronecker product

$$\begin{aligned} C_\mu^m &= [\mathbf{A}^t \times \mathbf{B}^s]_\mu^m \\ &= \sum_{\tau,\sigma} \langle t\tau s\sigma | m\mu\rangle A_\tau^t B_\sigma^s \qquad (42) \end{aligned}$$

with the standard notation for the vector coupling coefficients.[9] Then, the scattering equation (eq 35) can be written in the form

$$I_{\alpha\beta}^f = A\sum_{\gamma\delta} I_{\gamma\delta}^i \sum_{mnl} i^l(2l+1) \times$$
$$\langle j_l(K\mathbf{R}_{ab})[\mathbf{W}_{\alpha\gamma}^m\cdot\boldsymbol{\epsilon}^m(a)][\mathbf{W}_{\gamma\delta}^n\cdot\boldsymbol{\epsilon}^n(b)][\mathbf{C}^l(\hat{\mathbf{K}})\cdot\mathbf{C}^l(\hat{\mathbf{R}}_{ab})]\rangle \qquad (43)$$

recoupling these scalar products and making use of the fact that we are dealing with an isotropic system, we get the expression[3,4]

$$I_{\alpha\beta}^f = A\sum_{\gamma\delta} I_{\gamma\delta}^i \sum_{mnl} F^{mnl}\Phi^{mnl}(\alpha\beta,\gamma\delta) \qquad (44)$$

where

$$F^{mnl} = i^l\langle j_l(K\mathbf{R}_{12})\{[\boldsymbol{\epsilon}^m(1)\times\boldsymbol{\epsilon}^n(2)]^l\cdot\mathbf{C}^l(\hat{\mathbf{R}}_{12})\}\rangle \qquad (45)$$

$$\Phi^{mnl}(\alpha\beta,\gamma\delta) = \{[\mathbf{W}_{\alpha\gamma}^m \times \mathbf{W}_{\beta\delta}^n]^l\cdot\mathbf{C}^l(\hat{\mathbf{K}})\} \qquad (46)$$

This expression is analogous to that first derived by Ben-Reuven and Gershon,[3] and when $\alpha = \beta$ and $\gamma = \delta$ it becomes identical to their eq 20. In its general form, however, it has to be put in polar form (the greek indices are Cartesian) and also recoupled since the matrices **W** depend on incoming and outgoing polarizations simultaneously.

Therefore

$$[\mathbf{W}_{\alpha\gamma}^m \times \mathbf{W}_{\beta\delta}^n]^l = [(\mathbf{n}_\alpha^i\times\mathbf{n}_\gamma^f)^m \times (\mathbf{n}_\beta^i\times\mathbf{n}_\delta^f)^n]^l =$$
$$\sum_{s,t}[(2m+1)(2n+1)(2s+1)(2t+1)]^{1/2}\begin{Bmatrix} 1 & 1 & m \\ 1 & 1 & n \\ s & t & l \end{Bmatrix}\times$$
$$\{(\mathbf{n}_\alpha^i\times\mathbf{n}_\beta^i)^s \times (\mathbf{n}_\gamma^f\times\mathbf{n}_\delta^f)^t\}^l \qquad (47)$$

where we have used the standard notation for the $9-J$ symbols.[9]

Combining these equations, we can write the scattering

$$K_\sigma^s(f) = \sum_{t,\tau}\mathbf{S}_{\sigma\tau}^{st}K_\tau^t(i) \qquad (32)$$

equation in the desired form of eq 48 with the scattering matrix

$$\mathbf{S}_{\sigma\tau}^{st} = \sum_{mnl}[(2m+1)(2n+1)]^{1/2}\times$$
$$\begin{Bmatrix} 1 & 1 & m \\ 1 & 1 & n \\ s & t & l \end{Bmatrix} F^{mnl}\hat{\Phi}_{\sigma\tau}^{stl}(\Upsilon_i,\Upsilon_f,\hat{K}) \qquad (48)$$

where $\hat{\Phi}_{\sigma\tau}^{stl}$ is the rotational invariant defined by eq 7. This equation can be written in the form[4]

$$S_{\sigma\tau}^{st} = \sum_l \hat{\Phi}_{\sigma\tau}^{stl} G^{stl} \qquad (49)$$

$$G^{stl} = \sum_{mn}[(2m+1)(2n+1)]^{1/2}\begin{Bmatrix} 1 & 1 & m \\ 1 & 1 & n \\ s & t & l \end{Bmatrix} F^{mnl} \qquad (50)$$

Now, in the invariant $\hat{\Phi}_{\sigma\tau}^{stl}$, the arguments are not independent, and if we attach the reference frame to the vector $\hat{\mathbf{K}}$, then using the property of the irreducible representations (see eq 10), we can write

$$\mathbf{S}_{\sigma\tau}^{st} = \sum_x \Phi_{\sigma\tau,x}^{st}(\Upsilon_i,\Upsilon_\tau) G_x^{st} \qquad (51)$$

with

$$\Phi_{\sigma\tau,x}^{st} = [(2s+1)(2t+1)]^{1/2} D_{\sigma x}^s(\Upsilon_i) D_{\tau -x}^t(\Upsilon_f) \qquad (52)$$

and

$$G_x^{st} = \sum_l \begin{pmatrix} s & t & l \\ x & -x & 0 \end{pmatrix} G^{stl} \qquad (53)$$

The geometrical considerations needed for the transformations to the irreducible representations are described in Appendix A.

Let us now turn to the equation for the intensities (eq 33 and 34). Using eq 49, we get the invariant form of the cross section

$$S(\Upsilon_f) = \sum_{stl} \Psi^{stl}(\Upsilon_f) G^{stl} \qquad (54)$$

with

$$\Psi^{stl}(\Upsilon_f) = \sum_{\sigma,\tau} A_\sigma^s(f) K_\tau^t(i) \Phi_{\sigma\tau}^{stl}(\Upsilon_i, \Upsilon_f, \hat{\mathbf{K}}) \qquad (55)$$

and the molecular factor defined by (50). Alternatively, the irreducible representation yields

$$S(\Upsilon_f) = \sum_{st,x} \Psi_x^{st}(\Upsilon_f) G_x^{st} \qquad (56)$$

with

$$\Psi_x^{st}(\Upsilon_f) = \sum_{\sigma,\tau} A_\sigma^s(f) K_\tau^t(i) \Phi_{\sigma\tau,x}^{st} \qquad (57)$$

The scattering cross sections in eq 49, 51, 54, and 56 are alternative ways of writing one single functional form.

They all are made up by the sum of products of two factors: a photon, or geometrical factor, $\Psi(\Upsilon_f)$ and a molecular factor G^{stl}.

Quite independently from any model that is used to fit the data, as we will see in the forthcoming sections, there are only a few linearly independent molecular factors that could be involved, and which correspond to the correlations discussed in section I.

Therefore the possible patterns that one can obtain are necessarily limited. The functional form will be discussed in the next section.

IV. Angular Dependence for Plane Polarized Light

The equations of the last section are general and suited for any type of light, plane or circularly polarized.

A convenient way to process the experimental data is to find explicitly the values of the parameters K_μ^m or Stokes parameters of the scattered light, so that, for constant wave vector change K or scattering angle θ, the scattering cross sections $\mathbf{S}_{\sigma\tau}^{st}$ of eq 48 can be found as functions of the angles ζ and ψ. Then, using eq 51 one could find the irreducible molecular form factors G_x^{st}, which, as we will see in the next section, can be computed for model systems in a reasonably simple fashion. For plane polarized light, the invariants $\Phi_{\sigma\tau x}^{st}$ of eq 52 have been calculated in Appendix A.

However, the vast majority of the experimental data is presented in a different way,[1,2] and the quantities usually measured are the intensities scattered in configurations in which the polarizer and analyzer are either parallel (V_v) or perpendicular (H_v). Then, the invariant form of eq 54 is to be preferred. Making use of the relations of Appendix A, and after some heavy but straightforward algebra, we get for the parallel V_v scattering and in the absence of helical correlations eq 58.

This equation has terms with fourfold, twofold, and zerofold symmetry when we look at the ζ dependence.

From independent considerations,[3-5] we know that for $(KR) \rightarrow 0$, or the limit of either long wavelengths or short correlations, the terms with $l \neq 0$ vanish as $(KR)^l$. Therefore the only remaining terms are in eq 59, which exhibits the characteristic 8 shape (two-leaved clover) observed experimentally. The long range correlation contributions also

$$\begin{aligned} S_v = I_v^f/(AI_v^i) = {}& {}^1/_3\, G^{000} + \\ & G^{022}({}^1/_6\sqrt{2})[3(1 + \cos\theta)\cos^2\zeta - 2] + \\ & G^{202}({}^1/_6\sqrt{2})\left[\frac{3(1 + \cos\theta)\cos^2\zeta}{1 - \sin^2\theta\sin^2\zeta} - 2\right] + \\ & G^{220}\sqrt{5}\left[\frac{\cos^2\theta}{1 - \sin^2\theta\sin^2\zeta} - {}^1/_3\right] + \\ & G^{222}\sqrt{{}^5/_{14}}\left[{}^2/_3 + \frac{\cos^4\zeta\sin^2\theta\,(1 + \cos\theta) + \cos^2\zeta(\cos^3\theta - 2\cos\theta - 1)}{1 - \sin^2\theta\sin^2\zeta}\right] + \\ & G^{224}({}^1/_4)\sqrt{{}^5/_{14}}\left[2 + \frac{1}{1 - \sin^2\theta\sin^2\zeta}\{{}^1/_6\cos^4\zeta(25 + 60\cos\theta + 45\cos^2\theta + 10\cos^3\theta) - {}^1/_3\cos^2\zeta(9 + 25\cos 6 + 21\cos^2\theta + 5\cos^3\theta)\}\right] \end{aligned} \qquad (58)$$

have terms with fourfold symmetry. Therefore, we believe that the twofold symmetry is due mostly to the short ranged contributions of eq 59 which are also fully polarized.

$$S_v = {}^1/_3\, G^{000} + G^{220}\sqrt{5}\left[\frac{\cos^2\theta}{1 - \sin^2\theta\sin^2\zeta} - \frac{1}{3}\right] \qquad (59)$$

In the H_v configuration, the fully polarized components are cancelled, and the second term in eq 59 does not appear. The full equation yields

$$\begin{aligned} S_H = I_H^f/(AI_v^i) = {}& {}^1/_3 G^{000} + \\ & G^{022}({}^1/_6\sqrt{2})[3(1 + \cos\theta)\cos^2\zeta - 2] + \\ & G^{202}({}^1/_6\sqrt{2})\left[\frac{3(1 + \cos\theta)\sin^2\zeta}{1 - \cos^2\zeta\sin^2\theta} - 2\right] - G^{220}\sqrt{{}^5/_3} + \\ & G^{222}\sqrt{{}^5/_{14}}\left[{}^2/_3 + \frac{\cos\theta - 1 + \sin^2\theta\cos^2\zeta(2 - \cos^2\zeta(1 + \cos\theta))}{1 - \cos^2\zeta\sin^2\theta}\right] + \\ & G^{224}({}^1/_4)\sqrt{{}^5/_{14}}\left[2 + \frac{1}{1 - \cos^2\zeta\sin^2\theta} \times \{-3 - {}^5/_3\cos\theta - {}^1/_6\cos^4\zeta(25 + 60\cos\theta + 45\cos^2\theta + 10\cos^3\theta) + {}^1/_6\cos^2\zeta(43 + 70\cos\theta + 27\cos^2\theta)\}\right] \end{aligned} \qquad (60)$$

This is also a rather complicated equation. However, for systems with rather long correlations, such that $KR \geq 10$, then, even at small scattering angles ($\theta \sim 0.1$ rad), the correlations G^{222} and G^{224} will not vanish. But in the geometrical factor, only Ψ^{224} will retain an angular part for small angle $\theta \leq 0.1$

$$S_H \cong \text{constant} + \frac{5}{48}[2 - 5\cos^2\zeta + 7\cos^4\zeta]G^{224} \qquad (61)$$

This function has the shape of a four-leaved clover, the characteristic shape of the observed spectrum. Its "leaves", or maxima, are rotated by 45° from the polarization directions and do not depend explicitly on the details of the molecular or scattering units corelations.

V. Molecular Form Factors (the Case of Thin Rods)

Let us now turn to the molecular invariants defined by eq 45 and 50, F^{mnl} and G^{stl}. Since G^{stl} is a linear combination of the invariants F^{mnl}, we will only discuss the latter. Explicit relations for linearly polarized light and optically inactive systems are given in Appendix B.

In most experimental situations, F^{mnl} will be a function of the scattering angle θ, since it is a function of K

$$K = k_i \sin \theta_2 \tag{62}$$

(Notice, however, that we may change θ without changing K, just by adjusting the wave vector of the incident light, k_i. This can be done using, for example, a tunable laser.)

The explicit dependence of F^{mnl} on K depends on the structure of the material. For polymer systems, in which the size of the molecule or crystalytes is comparable or larger than the wavelength of the light, the calculation of this quantity may become rather cumbersome. Tagami[12] has performed such calculations and her results are rather involved, even in the simpler models.

We want to show that, if the irreducible representations of section I are used, then, surprisingly simple expressions are obtained.

Let us start out with the general expression of F^{mnl}, eq 45. From section I, we get after elementary transformations[3-5]

$$F^{mnl} = (i)^l(2l + 1)^{1/2} \sum_{\mu,\nu} \epsilon^m_\mu \epsilon^n_\nu (-)^{m+n+l} \times \sum_{\mu'\nu'\lambda'} \begin{pmatrix} m & n & l \\ \mu' & \nu' & \lambda' \end{pmatrix} \sum_{i,j} \langle j_l(\kappa \mathrm{R}_{ij}) C^l_{\lambda'}(\hat{\mathbf{R}}_{ij}) D^m_{\mu\mu'}(\Omega_i) D^n_{\nu\nu'}(\Omega_j)\rangle \tag{63}$$

where the polar components of the polarizability of the scattering units are defined by eq 2, 3, and 4. The scatterers (monomers, bonds) may be located in the same polymer molecule or crystalite or in different ones. The sum over (i, j) may be classified accordingly into the "self" and "distinct" contributions.

$$F^{mnl} = F^{mnl}_{(s)} + F^{mnl}_{(d)} \tag{64}$$

The "self" contribution can be calculated using eq 63 directly, since we suppose some definite (random) structure of the polymer molecule, with some known distribution function. The evaluation of the "distinct" part is somewhat more involved. Let us call α,β the two different polymer molecules on which the units i and j are located. The vectors $\mathbf{b}_{\alpha i}, \mathbf{b}_{\beta j}$ give the positions of the units within the molecules.

Clearly

$$\mathbf{R}_{ij} = \mathbf{R}_{\alpha\beta} + \mathbf{b}_{\alpha i} - \mathbf{b}_{\beta j} \tag{65}$$

Now the vector $\mathbf{R}_{ij}$ appears in eq 63 in the product of a spherical Bessel function and a spherical harmonic

$$j_l(K\mathbf{R}_{ij}) C^l_\lambda(\hat{\mathbf{R}}_{ij}) \tag{66}$$

Fortunately, a group theoretical method can be used to expand this particular combination. This was done by Nozawa[13] and the application to eq 66 is given in Appendix C. After substitution into eq 63 and some algebra, we get

$$F^{mnl}_{(d)} = [2l + 1]^{1/2} \sum_{rstj,\,pp'} (2t + 1)(2j + 1) \begin{Bmatrix} m & n & l \\ r & s & j \\ p & p' & t \end{Bmatrix} \begin{pmatrix} r & s & j \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} t & l & j \\ 0 & 0 & 0 \end{pmatrix} \sum_{\pi_1\pi_1'} A^{mr}_{p\pi_1} A^{*ns}_{p'\pi_1'} \mathbf{H}^{pp't}_{\pi_1\pi_1'}(K) \tag{67}$$

This expression relates the over-all "distinct" molecular form factor to the scattering form factors of the individual polymolecules $A^{mr}_{p\pi}$ and to the invariant coefficients of the polymer–polymer molecular, angle dependent correlation function $\mathbf{H}^{pp't}_{\pi_1\pi_1'}(K)$. The other factors in eq 67 are $3 - J$ and $9 - J$ symbols, in their standard notation.[9] The individual molecular form factors are defined by the expression

$$A^{mr}_{p_1\pi_1} = i^r(2r + 1)\langle j_r(K\mathrm{b}_{\alpha i})[\boldsymbol{\epsilon}^m(i) \times \mathbf{C}^r(\hat{\mathrm{b}}_{\alpha i})]^p_{\pi_1}\rangle \tag{68}$$

$$A^{*ns}_{p'\pi_1'} = i^{-s}(2s + 1)\langle j_s(K\mathbf{b}_{\beta j})[\boldsymbol{\epsilon}^n(j) \times \mathbf{C}^s(\hat{\mathrm{b}}_{\beta j})]^{p'}_{\pi_1'}\rangle \tag{69}$$

where the brackets $\langle\,\rangle$ indicate internal averages of the polarizabilities in the polymer molecule. As can be seen, the quantities $A^{mr}_{p\pi}$ are tensors of rank (p,π), while the quantities m,r refer to the make-up of the internal structure of the molecule. The molecular correlation function $\mathbf{H}^{pp't}_{\pi\pi'}(K)$ is defined as the Fourier–Bessel transform of the irreducible coefficients of the binary correlation function (eq 6).

$$\mathbf{H}^{mnl}_{\mu\nu}(K) = 4\pi i^l \int_0^\infty \mathrm{d}\mathbf{R}_{\alpha\beta}\mathbf{R}^2_{\alpha\beta} j_l(K\mathbf{R}_{\alpha\beta}) g^{mnl}_{\mu\nu}(\hat{\mathbf{R}}_{\alpha\beta}) \tag{70}$$

Equation 67 is still very complicated since it involves sums over eight indices. A considerably simpler expression can be obtained if the irreducible representation is used. In fact, defining (see eq 10)

$$F^{mn}_x = \sum_l \begin{pmatrix} m & n & l \\ x & -x & 0 \end{pmatrix} F^{mnl}(2l + 1)^{1/2} \tag{71}$$

we get, after some manipulations

$$F^{mn}_{(d)x} = \sum_{\substack{p\ \ p' \\ \pi_1\ \pi_1'}} \tilde{A}^{*mp}_{-x\pi_1} \tilde{A}^{np'}_{-x\pi_1'} \mathbf{H}^{pp'}_{\pi_1\pi_1'}(K) \tag{72}$$

where the irreducible form factors are defined from the invariants (eq 68 and 69) by

$$\tilde{A}^{mp}_{x\pi_1} = \sum_r \begin{pmatrix} p & m & r \\ x & -x & 0 \end{pmatrix} A^{mr}_{p\pi_1} \tag{73}$$

and we are using a slightly modified definition for the molecular correlation irreducible coefficient derived from eq 70.

$$\mathbf{H}^{pp'}_{\pi_1\pi_1',x}(K) = \sum_t \begin{pmatrix} p & p' & t \\ x & -x & 0 \end{pmatrix} (-)^t(2t + 1)\mathbf{H}^{pp't}_{\pi_1\pi_1'}(K) \tag{74}$$

Combining eq 64, 71, and 72, we get the final equation for the molecular form factor in the irreducible representation

$$F^{mn}_x = (F^{mn}_x)_{\mathrm{self}} + \sum_{\substack{p\ \ p' \\ \pi_1\ \pi_1'}} \tilde{A}^{mp}_{x\pi_1} \tilde{A}^{*np'}_{-x\pi_1'} \mathbf{H}^{pp'}_{\pi_1\pi_1'}(K) \tag{75}$$

In the most favorable case, we could get the invariants from experiment, but there is no *a priori* way of separating the self part of the scattering from the correlated "distinct" part.

If systems of the same polymer molecules can be made with different degrees of ordering, then, one could make reasonable guesses about the "form factors" $\tilde{A}^{mp}_{x\pi}$ and deconvolute or interpret in some way the correlation function irreducible coefficients $\mathbf{H}^{pp'}_{\pi\pi',x}(K)$. While this coefficient has been discussed in section I, let us remark here that the "chirality" or heliticity can be related directly to the experimentally observed one. Furthermore, in systems which have helices or helical correlations

$$F^{mn}_x \neq F^{mn}_{-x} \tag{76}$$

and the degree of heliticity can be directly measured, for example, by scattering circularly polarized light. For disordered systems like spherulitic polymer material, the correlated part is clearly negligible, in the sense that only $\mathbf{H}^{00}_{00,0}(K)$ exists. For oriented rods, however, both terms can be equally important. Let us compute the molecular invariants F^{mn}_x for this simple case. Suppose that the scattering units are cylindrically symmetric so that only ϵ^0_0 and ϵ^2_0 are nonzero. Suppose, furthermore, that the units are rotated by a constant amount from the rod-fixed axis, represented by the euler angles Ω_m. Then

$$F_{(s)}^{mnl} = \Sigma \epsilon_0^m \epsilon_0^n \frac{1}{2l + 1} D_{00}^l(\Omega_m) \rho_l(K) \qquad (77)$$

where we have used Tagami's notation[12] $\rho_l(K)$ for the intramolecular averages

$$\rho_l(K) = i^l \langle v^{-2} \sum_{i,j} j_l(K\mathrm{b}_{ij}) \rangle \qquad (78)$$

and, for thin rods, the explicit expressions can be found in ref 12. Similarly, the form factors (eq 73) are given by

$$\widetilde{A}_{x\pi_1}^{mp} = (2p + 1)\epsilon_0^m D_{0-\pi_1}^m(\Omega_m) Z_p(K) \qquad (79)$$

with the intramolecular average

$$Z_p(K) = i^p \frac{1}{v} \sum_i j_p(K\mathrm{b}_{\alpha i}) \qquad (80)$$

which is the Fourier–Bessel transform of the density of scattering units taken as a function of the position inside the molecule.

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Appendix A

Light Scattering Geometry. If we attach the reference frame to the incoming light, in the geometry of section II, the vectors are given by incoming light, $\Upsilon^i = (0, 0, 0)$

$$\mathbf{n}_1^i = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}; \quad \mathbf{n}_2^i = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}; \quad \mathbf{k}_0 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \qquad (A.1)$$

scattered light, $\Upsilon^f = (\zeta, \theta, \psi)$

$$\mathbf{n}_1^f = \begin{pmatrix} \cos\theta \cos\zeta \cos\psi - \sin\zeta \sin\psi \\ \cos\theta \sin\zeta \cos\psi + \cos\zeta \sin\psi \\ -\sin\theta \cos\psi \end{pmatrix} \qquad (A.2)$$

$$\mathbf{n}_2^f = \begin{pmatrix} -\cos\theta \cos\zeta \sin\psi - \sin\zeta \cos\psi \\ -\cos\theta \sin\zeta \sin\psi + \cos\zeta \cos\psi \\ \sin\theta \sin\psi \end{pmatrix} \qquad (A.3)$$

$$\mathbf{k}_f = \begin{pmatrix} \sin\theta \cos\zeta \\ \sin\theta \sin\zeta \\ \cos\theta \end{pmatrix} \qquad (A.4)$$

From here

$$\hat{\mathbf{K}} = \begin{pmatrix} -\cos\theta/2 \cos\zeta \\ -\cos\theta/2 \sin\zeta \\ \sin\theta/2 \end{pmatrix}$$

$$|K| = k_i \sin\theta/2 \qquad (A.5)$$

or

$$\Upsilon_K = (\zeta, (\theta - \pi)/2, 0)$$

gives the orientation of the vector $\hat{\mathbf{K}}$. Now performing the inverse rotation $R^{-1}(\Upsilon_K)$ to the rigid system of the incoming and outgoing radiation frames we get

$$\Upsilon_i^k = (-\zeta, (\pi - \theta/2), 0) \qquad (A.6)$$

$$\Upsilon_f^k = (\psi, (\pi + \theta)/2, 0) \qquad (A.7)$$

Now in the polymer film experiments of Stein and coworkers,[1] the analyzer and polarizer are kept either parallel or perpendicular to each other.

In the first case V_v, $\mathbf{n}_1^i$, and $\mathbf{n}_1^f$ are perpendicular to $\mathbf{n}_2^i$ at all times. Therefore, the angle ψ is determined by the condition

$$\mathbf{n}_2^i \cdot \mathbf{n}_1^f = 0 \qquad (A.8)$$

or

$$\cos\theta \sin\zeta \cos\psi = -\cos\zeta \sin\psi \qquad (A.9)$$

which is satisfied if

$$\sin\psi = -\cos\theta \sin\zeta\{1 - \sin^2\zeta \sin^2\theta\}^{-1/2} \qquad (A.10)$$

$$\cos\psi = \cos\zeta\{1 - \sin^2\zeta \sin^2\theta\}^{-1/2} \qquad (A.11)$$

In the second case we require

$$\mathbf{n}_1^i \cdot \mathbf{n}_1^f = 0 \qquad (A.12)$$

or

$$\cos\theta \cos\zeta \cos\psi = \sin\zeta \sin\psi \qquad (A.13)$$

with

$$\sin\psi = \cos\theta \cos\zeta\{1 - \cos^2\zeta \sin^2\theta\}^{-1/2} \qquad (A.14)$$

$$\cos\psi = \sin\zeta\{1 - \cos^2\zeta \sin^2\theta\}^{-1/2} \qquad (A.15)$$

For plane polarized light, the indices $s\sigma(t,\tau)$ can only take values of 0,±2. Then, using the coefficients for plane polarized light (eq 31), the irreducible representation geometrical form factors are

$$\psi_0^{00} = 1/3 \qquad (A.16)$$

$$\psi_0^{02} = \frac{1}{6}\sqrt{\frac{5}{2}}[3(1 + \cos\theta)\cos^2\zeta - 2] \qquad (A.17)$$

$$\psi_0^{20} = \frac{1}{6}\sqrt{\frac{5}{2}}[3(1 + \cos\theta)\cos^2\psi - 2] \qquad (A.18)$$

$$\psi_0^{22} = \frac{5}{24}[3(1 + \cos\theta)\cos^2\zeta - 2][3(1 + \cos\theta)\cos^2\psi - 2] \qquad (A.19)$$

$$\psi_{\pm1}^{22} = \frac{5}{4}[\sin\theta \cos^2\psi \mp i \cos\theta/2 \sin^2\psi] \times [\sin\theta \cos^2\zeta \pm i \cos\theta/2 \sin 2\zeta] \qquad (A.20)$$

$$\psi_{\pm2}^{22} = \frac{5}{16}[(3 - \cos\theta)\cos^2\psi - 2 \mp 2i \sin\theta/2 \sin 2\psi][(3 - \cos\theta)\cos^2\zeta - 2 \pm 2i \sin\theta/2 \sin 2\zeta] \qquad (A.21)$$

Appendix B

Relations between the Invariants *G* and *F*. For linearly polarized light, $s,t = 0,2$; therefore, eq 50 is, explicitly

$$G^{000} = \frac{1}{3}F^{000} + \frac{\sqrt{5}}{3}F^{220} \qquad (B.1)$$

$$G^{220} = \frac{1}{3\sqrt{5}}F^{000} + \frac{1}{30}F^{220} \qquad (B.2)$$

$$G^{202} = \frac{\sqrt{5}}{3}(F^{202} + F^{022}) + \frac{1}{6}\sqrt{\frac{7}{5}}F^{222} \qquad (B.3)$$

$$G^{022} = \frac{\sqrt{5}}{3}(F^{202} + F^{022}) + \frac{1}{6}\sqrt{\frac{7}{5}}F^{222} \qquad (B.4)$$

$$G^{222} = \frac{\sqrt{7}}{30}(F^{202} + F^{022}) - \frac{1}{30}F^{222} \qquad (B.5)$$

$$G^{224} = \frac{1}{5}F^{224} \qquad (B.6)$$

Equally simple relations can be derived for the irreducible representations G_x^{st} and F_x^{mn}

Appendix C

The Expansion of Solid Bessel Functions. The function $j_l(x)\, C_\lambda^l(\hat{\mathbf{x}})$, where $\mathbf{x}$ is a vector of modulus x and orientation $\hat{\mathbf{x}} = \theta_x, \zeta_x$ is sometimes called a solid spherical bessel function.[13] Quite clearly

$$j_l(\mu\mathbf{R}_{ij})C_\lambda^l(\hat{\mathbf{R}}_{ij}) = \frac{(-i)^l}{4\pi}\int \mathrm{d}\mathbf{K}e^{i\mathbf{K}\cdot\mathbf{R}_{ij}}C_\lambda^l(\hat{\mathbf{K}})\frac{\delta(\mu - K)}{\mu K} \tag{C.1}$$

where $\delta(x)$ is the Dirac δ function. But, we have

$$\mathbf{R}_{ij} = \mathbf{R}_{\alpha\beta} + \mathbf{b}_{\alpha i} - \mathbf{b}_{\beta j} \tag{65}$$

Therefore, replacing and making repeated use of Rayleigh's expansion formula (eq 39), we get, after much algebra

$$\begin{aligned} j_l(\mu\mathbf{R}_{ij})C_\lambda^l(\hat{\mathbf{R}}_{ij}) = {} & \\ & (-i)^l\sum_{rst}(i)^{r+s+t}(2r + 1)(2s + 1)(2t + 1) \times \\ & j_r(\mu\mathbf{b}_{\alpha i})j_s(\mu\mathbf{b}_{\beta j})j_t(\mu\mathbf{R}_{\alpha\beta})\sum_{p\sigma\tau} C_p^r(\hat{\mathbf{b}}_{\alpha i})C_\sigma^s(\hat{\mathbf{b}}_{\beta j}) \times \\ & C_\tau^t(\hat{\mathbf{R}}_{\alpha\beta})(-)^\tau\sum_{j,\zeta}(2j + 1)\begin{pmatrix} r & s & j \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} t & l & j \\ 0 & 0 & 0 \end{pmatrix} \times \\ & \begin{pmatrix} r & s & j \\ p & \sigma & -\zeta \end{pmatrix}\begin{pmatrix} t & l & j \\ \tau & \lambda & \zeta \end{pmatrix} \end{aligned} \tag{C.2}$$

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The Determination of Chain Statistical Parameters by Light Scattering Measurements

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ABSTRACT: The effects of volume exclusion on polymer chain conformations can be determined from the study of the angular dependence of radiation scattered by chain molecules. It is found that useful information can be obtained only when the variable x is large, where x is the product of the square of the magnitude of the scattering vector and of the mean square radius of gyration. Hence, solutions of macromolecules of very high molecular weight are needed for these investigations. The theoretical treatment of the scattering function is based on several assumptions. The validity of these assumptions is examined by computing, using a Monte-Carlo technique, various moments of intramolecular separations and comparing the results so obtained, in the limit of a chain of infinite length, with the analytical results. The computations seem to verify the validity of the theoretical model. The scattering behavior of solutions of recently synthesized polystyrene of $M_w = 4.4 \times 10^7$ in cyclohexane at various temperatures and in benzene at 40° was investigated. From the log–log plots of the scattering function vs. x, a statistical parameter was calculated, whose value depends on the magnitude of long-range correlations between any pair of chain elements. It is found that above the Θ temperature this parameter is practically independent of temperature and that its numerical value was found to agree well with the value obtained from Monte-Carlo calculations. In the neighborhood of the Θ temperature, this parameter decreases rapidly with decreasing temperature, indicating a first-order transition in chain conformation.

I. Introduction

A. Experimental Background. Since the introduction of Debye's analysis[2] of molecular light scattering measurements, it has been the mainstay of exacting studies of polymeric chain dimensions and their parametric dependence on molecular weight and excluded volume. In particular, its use for the determination of the weight average molecular weight and the z average radius of gyration has become routine and totally accepted. These routine determinations, however, only utilize a small portion of the available scattering pattern. Much less common is experimental and theoretical work that attempts to use as much of the scattering pattern as can be experimentally determined. Indeed a recent review[3] as well as other research papers imply that there is considerable uncertainty about what new information on chain statistics can be experimentally determined.

Therefore this paper attempts (1) to show more incisively than before what information from the experimentally accessible scattering curve can reasonably be related to the statistical description of the chain from either Monte-Carlo or chain enumeration methods, (2) to interpret newly available light scattering measurements on polystyrene in good and poor solvents to calculate these same chain statistical parameters, and (3) to demonstrate that a better knowledge of the chain statistical parameters is not likely to be obtained unless molecules which are chemically tagged at definite intervals to enhance scattering are used in scattering measurements.

Typical chain dimensions are usually expressed as end-to-end distance or radius of gyration. Over the whole polymer of N segments these distances will be respectively designated r_N and S_N. There is considerable evidence, based on both Monte-Carlo investigations and exact chain enumerations, which shows that r_N^2 and S_N^2, when averaged over all configurations, depend on molecular weight, M, as