Interparticle Interference in Light Scattering from Spherulitic Systems

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ABSTRACT: The use of lasers for recording H_v light scattering patterns from spherulitic systems gives rise to interspherulitic interference effects due to coherence of the beam. This is illustrated in this paper, and model experiments using starch granules and isotactic polystyrene spherulites in specific configurations are reported. Under such conditions, interspherulitic interference gives rise to predictable diffraction phenomena in the H_v patterns which are responsible for the "speckled" appearance of laser-generated light scattering patterns from collections of spherulites.

The theoretical description of light scattering from isolated spherulites has been thorough.[2,3] This theory has been used to account for experiments in which, for the most part, scattering was observed from films completely filled with spherulites. Even though interspherulitic interference would be expected to affect the scattering from such films—especially with highly coherent (laser) sources—the gross features of the experimental H_v patterns are well decribed[2b] by the theory for isolated spherulites. (H_v is a notation which refers to the experimental geometry wherein the incident beam is vertically polarized and the scattered rays are analyzed through a horizontal analyzer.) A close examination of the experimental pattern for an assembly of isotactic polystyrene spherulites (*cf.* Figure 1) shows that the fine structure of the pattern is quite different from that of an isolated spherulite. A theoretical treatment of interference effects from a statistically described, liquid-like distribution of spherulite centers[4] has already been presented and can be used to account, qualitatively, for the variation of scattering intensity during spherulite growth.[5] Because this theory for statistical distributions has some shortcomings resulting from the unrealistic distribution of nuclei and neglect of impingement of growing spherulites, we have reexamined the theory of interspherulitic interference by considering particles whose location is well defined. The origin of "speckles" in laser-generated scattering experiments has been discussed for translucent diffusers.[6]

This kind of approach was suggested by observations made with pairs of starch granules arranged in a definite geometry with respect to the vertical polarization plane of the incoming laser beam.[7] Two adjacent granules of tapioca starch mounted in Canada balsam yielded the pattern shown in Figure 2. The expected cloverleaf envelope is modulated by interference fringes whose orientations are normal to the line joining the particle centers.

The theory for such scattering behavior was developed by using the general expression for the light scattered by an assembly of interfering particles

$$I = KEE^* = K\sum_m\sum_n E_m E_n^* \exp[ik(\mathbf{D}_{mn}\cdot\mathbf{s})] \qquad (1)$$

where K is a numerical factor, E is the scattered amplitude, E^* is the complex conjugate of the scattered amplitude, and $\mathbf{D}_{mn}$ is the vector separation of the centers or arbitrary origins of two particles; as usual $k = 2\pi/\lambda$, where λ is the wavelength in the medium, and $\mathbf{s}$ is the propagation vector equal to $\mathbf{s}_0 - \mathbf{s}'$ in the usual notation for the unit vectors describing the incident and scattered light beams. In the case of a pair of particles, eq 1 reduces to

$$I = I_{s_1} + I_{s_2} + KE_1E_2^* \exp[ik(\mathbf{D}_{12}\cdot\mathbf{s})] + KE_2E_1^* \exp[-ik(\mathbf{D}_{12}\cdot\mathbf{s})] \qquad (2)$$

where I_{s_1} and I_{s_2} are the intensities scattered by isolated particles 1 and 2 (*cf.* Figure 4).

Our calculations using eq 2 were restricted to the case of two-dimensional spherulites in order to be able to easily take into account the truncation effect which can occur when $\mathbf{D}_{12}$ is smaller than $2R$ (R is the radius of the spherulites). By using the parameters defined previously one can write

$$k(\mathbf{D}_{12}\cdot\mathbf{s}) = WG\cos(\mu - \gamma) \qquad (3)$$

where

$$G = \mathbf{D}_{12}/R \qquad W = (2\pi/\lambda)\sin\theta$$

where γ is the angle between the line joining the particle centers and the vertical (see Figure 4); as usual, θ and μ are the scattering and azimuthal angles, respectively. E_1, E_2, I_{s_1}, and I_{s_2} were evaluated according to the method described in a previous paper,[8] which consists of the case of impingement of the spherulites, of subtracting the amplitudes of the truncated portions from the amplitudes of the complete particles.

Model experiments have been carried out by using isotactic

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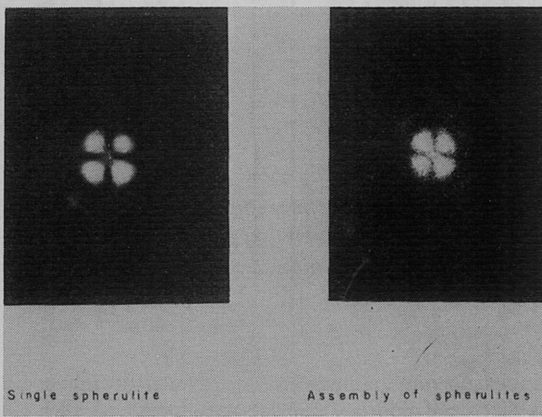

Figure 1. An experimental scattering pattern from a single isotactic polystyrene spherulite and from a volume-filling assembly of the same spherulites.

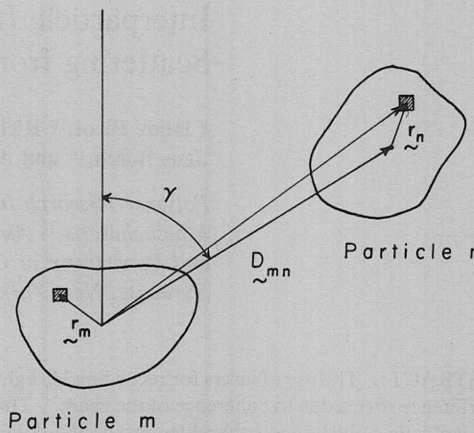

Figure 4. The parameters describing the scattering from a pair of particles whose centers are separated by a distance D and where **r** is the vector coordinate of a scattering element within the particle and with respect to its center.

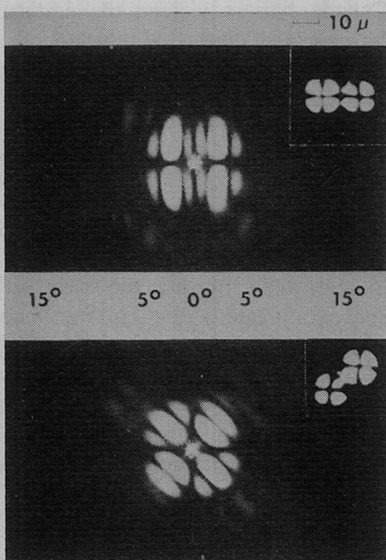

Figure 2. H_v scattering envelopes from two adjacent tapioca starch granules of similar size. Photomicrographs, crossed nicols, are shown (right insert). Equatorial scattering, θ, is indicated.

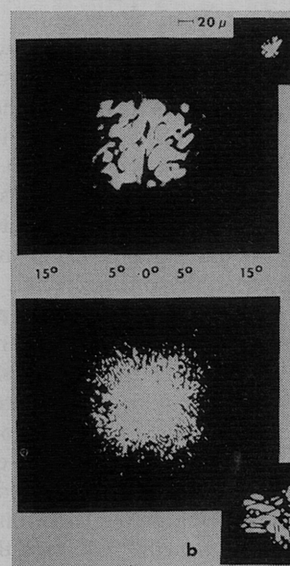

Figure 5. H_v scattering envelopes from clusters of tapioca (a) and potato starch granules (b). Photomicrographs, crossed nicols, are shown (right insert). Equatorial scattering angle θ is indicated.

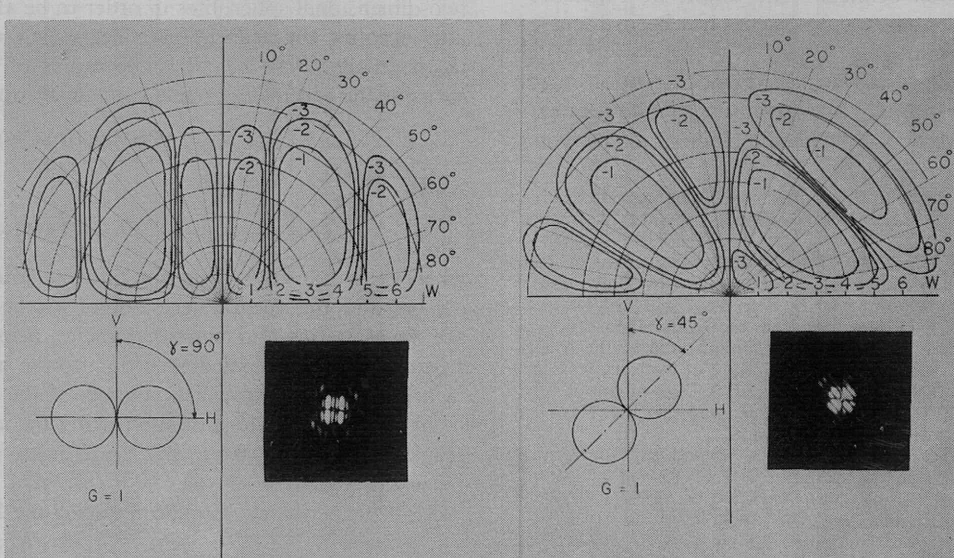

Figure 3. The theoretical and experimental scattering patterns from a pair of spherulites for which the lines joining the centers are at angle γ of 90 and 45°.

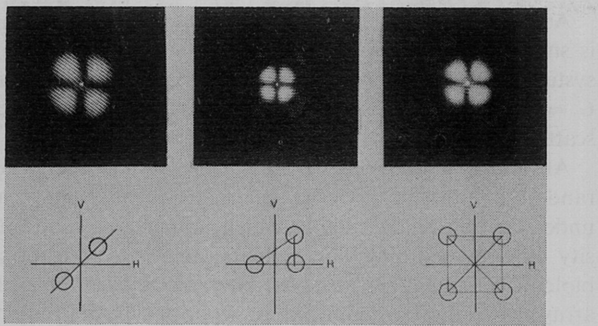

Figure 6. Experimental scattering patterns resulting from some elementary arrays of spherulites.

polystyrene films whose crystallization was stopped before completion by quenching at room temperature. Then, sets of spherulites have been selected and isolated from the others by dissolution of the amorphous surrounding. Such spherulites are essentially disklike and satisfy the two-dimensional limitation imposed in the theory. Similarly, starch granules of various sizes and shapes[7,9] are valuable models because their scattering configuration is readily manipulated.

Figure 3 shows the theoretical and experimental scattering envelopes for two isotactic polystyrene spherulites, where the vectors joining the spherulite centers have the same orientation as for the starch granules in Figure 2. Clearly, theory and experimentation are in good agreement and the effect of interspherulitic interference is to add additional features to the scattering pattern which, when not properly controlled, can severely limit the information normally obtainable from it. An extreme example of this is shown in Figure 5, which depicts scattering patterns from clusters of starch granules where individual particles are not in a random configuration. The pattern in Figure 5a resembles the optical transform of an asymmetric scattering object, while Figure 5b shows an

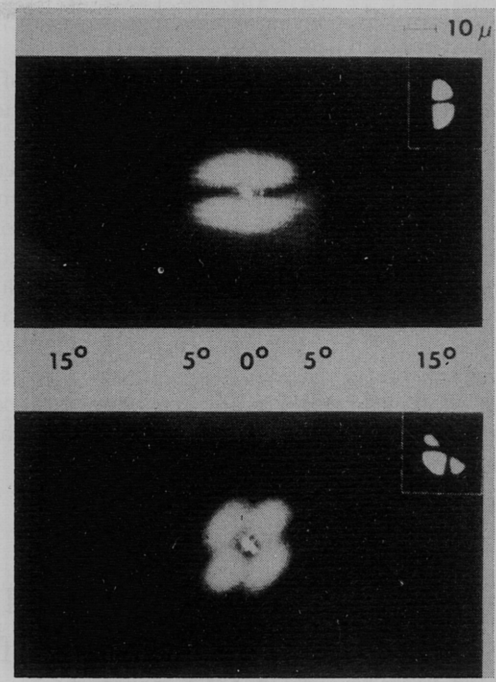

Figure 7. H_v scattering envelopes from an asymmetric tapioca starch granule. Photomicrographs, crossed nicols, are shown (right insert). Equatorial scattering angle, θ, is indicated.

A good theoretical understanding of the interspherulitic interference effects is now possible. The theory summarized above has been applied to explain the scattering which arises from polystyrene spherulites arranged in specific configurations as shown in Figure 6. An important feature of Figure 6 is the pronounced fringe pattern which is superimposed on the classical four-leaf-clover envelope when only two spherulites are present. Diffraction specialists will readily recognize

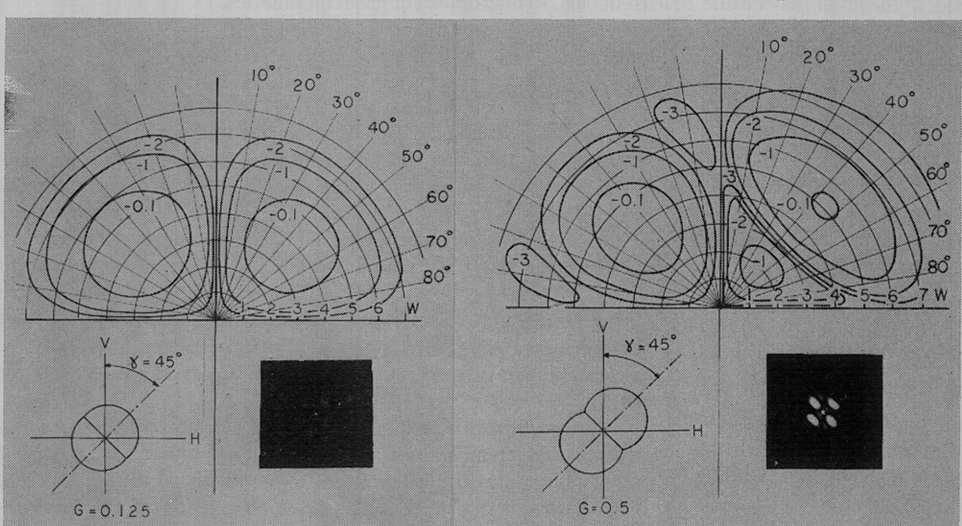

Figure 8. Theoretical and experimental scattering pattern from pairs of impinging spherulites of differing separation as given by the parameter *G*.

incipient cloverleaf with the speckling which has been a feature of many photographic light scattering patterns recorded with laser sources for a collection of particles.[10] There is no doubt that for a truly random location of the spherulite nuclei a "random modulation" of the scattered intensity will result; this can explain the speckling of the patterns observed for an assembly of spherulites or starch granules.

the convolution of a lattice and an object transform, the individual spherulite centers being the lattice points. The speckled appearance in Figure 6 when four spherulites are present is in reality a diffraction pattern from a near-tetragonal arrangement of spherulites. However, when the objects are not perfect spherulites,[8] scattering along the equatorial and meridional directions results, and this is contrary to theory for scattering from a single spherulite.

When the fringe pattern is well defined, it can be a useful measure of center-to-center distance in regularly arranged spherulite systems, the interparticle distance being given by a

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well-known formula. Obviously, the frequency of the modulation increases with the interparticle distance.

Aside from explaining the speckled appearance of laser-generated light scattering photographs from collections of spherulites, the present approach is quite useful in understanding effects, such as mutual truncation of spherulites, which are illustrated experimentally in Figure 7, using half sections of tapioca starch granules in two different orientations. Clearly this has the effect of producing considerable scattering on the equator and meridian of the scattering envelopes, whereas the ideal spherulite does not scatter at these positions. When truncation results from impingements of growing spherulites in a volume-filling assembly of spherulites whose full radius is R, and where the distance between nuclei is smaller than $2R$, the above theory predicts the scattering envelope shown in Figure 8.

As could be expected when the separation between nuclei is small in comparison to the spherulite radii, the scattering system tends to behave like a single particle (see Figure 8, $G = 0.125$). The top part of Figure 8 corresponds to the scattering envelope for the systems shown.

An understanding of this general problem of scattering by random or mutually ordered spherulites is pertinent to a full understanding of the factors which influence absolute intensity in volume-filling spherulite systems. Applications to biological systems where spherulites often occur in ordered array, as in the bordered pits of wood tracheids, require an understanding of interspherulitic interference effects.[11]

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Diffusion and Solubility of Simple Gases through a Copolymer of Hexafluoropropylene and Tetrafluoroethylene

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ABSTRACT: The transport of seven gases, N_2, O_2, CO_2, CH_4, C_2H_6, C_3H_8, and C_2H_4, through FEP, a copolymer of hexafluoropropylene and tetrafluoroethylene, has been studied systematically over a temperature range of about 25–85°. For all the gases studied, linear Arrhenius plots of both permeation and diffusion coefficients were obtained. Empirical linear correlations both between the logarithm of the solubility at 25° and the heat of solution, and the Lennard-Jones force constant of the gases, were found. Furthermore, the standard entropies of solution and of diffusion were linearly dependent on the associated enthalpies. A comparison of the FEP data with those for polyethylene taken from the literature points up the limitations of existing theories of transport through polymers. Finally, the comparison with data on polytetrafluoroethylene (PTFE) indicates that the properties of the latter may be due, at least in part, to micropores or grain boundaries.

In a recent study of gas transport in polytetrafluoroethylene (PTFE) it was found that the activation energies of diffusion of N_2, O_2, and CO_2 were approximately 2 kcal/mol lower than they were in polyethylene (PE).[1] Since complete fluorination of polyolefins leads to considerable stiffening of the carbon backbone, this is an unexpected result which suggests that diffusion progresses partly through micropores in the PTFE. Such an explanation appears reasonable since PTFE of sufficiently high molecular weight to be usable virtually does not flow in the melt above its crystalline melting point of 327° because of its extremely high viscosity; fabrication requires compacting PTFE powder under high pressure near room temperature and then sintering at temperatures around 380°. The final product usually obtained by machining very likely contains micropores.

The present study of diffusion through a copolymer of hexafluoropropylene and tetrafluoroethylene (FEP) was undertaken partly to verify this postulated diffusion mechanism. FEP has a crystalline melting point near 290° and, whereas it retains most of the properties of PTFE, it has a melt viscosity in a range which allows fabrication by conventional techniques. Thus, FEP films can be expected to be free of micropores.

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Experimental Section

Measuring Method. The dynamic method for measuring permeation and diffusion rates of gases and vapors in polymer membranes and the evaluation of the permeation and diffusion coefficients from the raw data have been described in detail elsewhere.[2,3] The instrument used here was an engineering model of the polymer permeation analyzer (manufactured by Infotronics Instrument Corp., Mountain View, Calif.). This instrument is equipped with three permeation cells, which can accept membranes of different thickness, and thus it permits a wide choice of measuring conditions. A low-volume valve permits selection of any of the three cells for study.

The instrument is well suited to rapid study of a series of gases over a wide temperature range. In actual operation, a gas at atmospheric pressure is admitted from a manifold to the upstream side of the thermostated cells; after completion of the measurements, the manifold is evacuated with a mechanical pump, another gas is admitted, and the procedure is repeated.

As a test of reproducibility, the permeation rates of CO_2 at 35° through one piece of FEP mounted across all three cells were measured. They were found to agree within 2%, which is equal to the reproducibility of repeat measurements for one cell.

The concentration of permeant gas in the helium carrier gas sweeping past the membrane was measured with a katharometer. The absolute detector sensitivity for CO_2 was determined by means of a CO_2–He mixture of known concentration. The sensitivities

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