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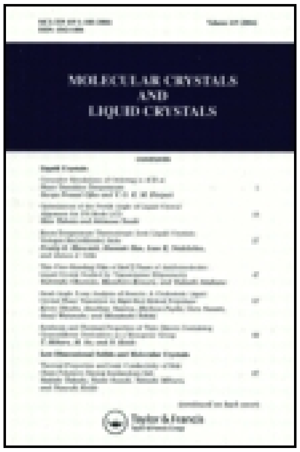

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The Specification of Order in Mesophases

Richard S. Stein [a]

[a] Polymer Research Institute and Department of Chemistry, University of Massachusetts, Amherst, Massachusetts, 01002

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The Specification of Order in Mesophases‡

RICHARD S. STEIN

**Polymer Research Institute and Department of Chemistry
University of Massachusetts
Amherst, Massachusetts 01002**

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Abstract—The description of order in mesophases in terms of angularly dependent radial distribution functions and in terms of correlation functions in density and orientation is discussed. The determination of these functions from light scattering and diffraction data is described. The concept of non-randomness of orientation correlations is introduced and its description in terms of non-randomness parameters or correlation functions is proposed. It is pointed out that mesophases of complex structure may be defined in terms of parameters describing the amplitudes and correlation distances for the correlations in density and in random and non-random orientation. The most striking changes at mesophase transitions are in the randomness of the orientation correlations. The relationship between the correlation functions and the morphology for model systems is illustrated.

Introduction

Mesophases or " liquid crystals " are characterized by the existence of long range order intermediate between that in the liquid and crystalline states.[1] The nature of such order has been generally classified into such categories as smectic, nematic, and cholesteric with the definitions dependent upon the type of

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molecular organization. It has become evident that such classification is too restrictive in that variations in structure exist within these categories. Furthermore, each of these structures are characterized by unique directions for the molecular axes. These directional orientations may not persist to the same degree throughout the mesophase so as to lead to macroscopic orientation. There is rather a domain structure of a statistically defined size, within which there is a tendency toward orientation. However, these domains may be randomly oriented with respect to each other. More quantitative characterization of the orientation is thus required to specify such structure.

Radial Distribution Functions

The structure of a liquid or a crystal can often be specified in terms of radial distribution functions of atomic centers or electron density, $g(r)$[2]. These are periodic damped functions of distance and express the fact that it is more probable to find other atoms and molecules at some distances than others. The first maximum away from the center corresponds to the nearest neighbor distance, the next to the second nearest neighbor, etc. From the radial distribution function of electron density, it is possible to calculate the intensity of diffracted X-rays.

Liquids differ from crystals in that their radial distribution function damps much more rapidly indicating a " washing-out " of order as a result of the randomness of structure.

Mesophases may also be characterized by a radial distribution function which will be intermediate between that of a solid and a liquid. Such functions will depend upon temperature but will undergo sharp changes at mesophase transition temperatures.

While liquids have spherical symmetry, crystals generally do not and the radial distribution function will depend on the vector distance, $\mathbf{r}$, being a function of the angular coordinates α and ϕ, of location of a particular point.

In this case, the scattering intensity will no longer be cylindrically symmetrical about the incident beam but will depend upon an azimuthal coordinate, $\Omega^{4,5}$ (Fig. 1). Thus, the variation of I with Ω is a measure of the dependence of $g(\mathbf{r})$ upon α.

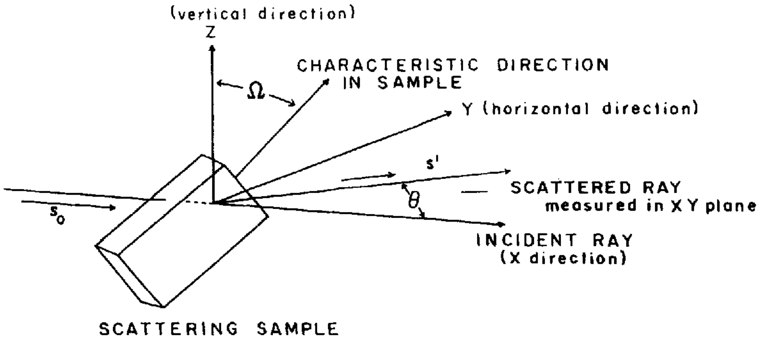

Figure 1. The coordinates θ, Ω, and ϕ defining the scattering direction.

For liquids, spherical symmetry persists in the time-average. Again, mesophases are intermediate in behavior. If the coordinate system is chosen such that the coordinate axes correspond to the principal axes of orientation of a given region within the mesophase, angular dependence of $g(\mathbf{r})$ will persist so long as r is smaller than the average radius of an oriented domain. However, if r is bigger than this, then since different domains will be oriented randomly with respect to each other, there will be little angular dependence of $g(\mathbf{r})$. Of course, the domain boundaries are somewhat arbitrary as they are statistical in nature. Mesophases will therefore differ from crystals in that the angular dependence of $g(\mathbf{r})$ will decay much more rapidly with increasing r.

The situation in a crystal is static while that in a mesophase is in a dynamic state with the domain boundaries and orientation directions continually changing. A diffraction or scattering experiment sees the average situation over the time of measurements. If one examines the scattering from a sufficiently small volume of sample (containing only a few domains) for a sufficiently short time (less than that of the domain orientation relaxation time, τ), the scattering will depend upon Ω indicating a dependence of $g(\mathbf{r})$ upon α. This dependency is lost for larger scattering volume elements and for longer τ's. This is especially true at small scattering angles, θ, as these correspond to scattering at large $|\mathbf{r}|$ where the α dependence is less.

In the foregoing discussion it was assumed that there was no macroscopic orientation so that the domains of the mesophase were oriented randomly with respect to an external coordinate system and with respect to each other. If an orienting field such as electrostatic, magnetic, or mechanical shear is applied, the domain orientation axis will rotate and orient with respect to the field. A steady-state orientation distribution will result which will give rise to a steady-state Ω dependence of $I(\alpha, \phi)$ independent of τ.

If the applied field is oscillatory, the orientation axis will oscillate in direction with an amplitude and phase lag dependent upon the relationship between the frequency of oscillation, ω, and the orientation relaxation frequency of the system. Thus there will be a frequency dependence of the scattering response (dynamic scattering) which will characterize the structural mobility of the system. The structural mobility of mesophases will be intermediate between that of liquids and crystals and will change discontinuously at mesophase transitions. A preliminary discussion of the theory of dynamic light scattering has appeared[6] and an apparatus for its measurement has been designed and constructed.[7]

At large distances, the value of $g(\mathbf{r})$ approaches that of the average electron density g_0 (which is often subtracted out in the plots). Thus the fluctuation in electron density

$$\xi(\mathbf{r}) = g(\mathbf{r}) - g_0 \qquad (1)$$

approaches zero in its time average at large r. While its time-average value is zero, its instantaneous value is not so that at large r $\xi(r)$ will fluctuate from zero through small positive and negative values. Such fluctuation will be much greater in the liquid than the solid state. It is apparent that mesophases will also be intermediate in this behavior between that of solids and liquids.

Density Correlations

The scattering (or diffraction) intensity may be formulated in terms of $\xi(\mathbf{r})$ to give

$$I(\theta, \Omega) = K_x \iiint \Gamma(\mathbf{r}_{12}) \cos[k(\mathbf{r}_{12} \cdot \mathbf{s})]\, r_{12}^2 \sin\alpha_{12}\, dr_{12}\, d\alpha_{12}\, d\phi_{12} \quad (2)$$

where

$$\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2 \quad (3)$$

is the vector separation of scattering elements 1 and 2 located by vectors $\mathbf{r}_1$ and $\mathbf{r}_2$. α_{12} and ϕ_{12} are the angular coordinates of $\mathbf{r}_{12}$ (Fig. 2).

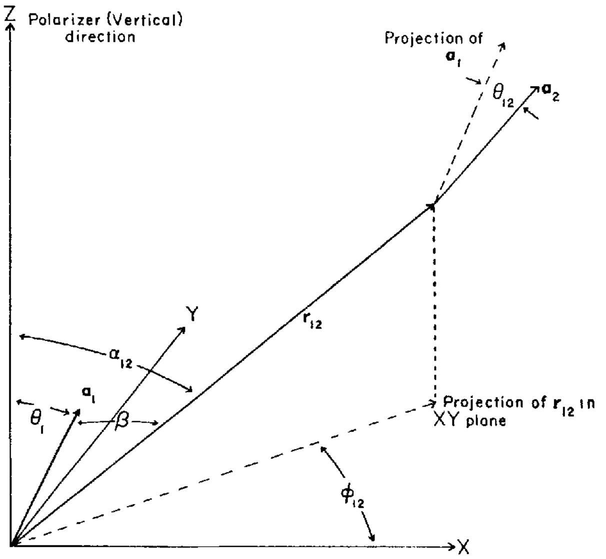

Figure 2. The coordinates of a pair of scattering elements and their principal polarizability directions.

$\Gamma(\mathbf{r}_{12})$ is an electron density fluctuation correlation function defined by

$$\Gamma(\mathbf{r}_{12}) = \frac{\langle \xi(\mathbf{r}_1)\, \xi(\mathbf{r}_2)\rangle_{\mathbf{r}_{12}}}{\langle [\xi(r_1)]^2\rangle_{\text{av}}} \quad (4)$$

E

The symbol $\langle\ \rangle_{\mathbf{r}_{12}}$ designates a time and space average over all pairs of volume elements separated by $\mathbf{r}_{12}$ whereas $\langle\ \rangle_{\mathrm{av}}$ designates a time and space average over all volume elements. For spherically symmetrical systems $\Gamma(\mathbf{r}_{12})$ is independent of α_{12} and ϕ_{12}. A scaler correlation function may be defined as

$$\Gamma(r_{12}) = \int \Gamma(\mathbf{r}_{12}) \sin \alpha_{12}\, d\alpha_{12}\, d\phi_{12} = 4\pi \Gamma(\mathbf{r}_{12}) \tag{5}$$

and Eq. (2) reduces to

$$I(\theta, \Omega) = 4\pi K_x \int \Gamma(r_{12}) \frac{\sin(hr_{12})}{hr_{12}} r_{12}^2\, dr_{12} \tag{6}$$

$\Gamma(r_{12})$, like $g(r)$ may be obtained by a Fourier inversion of Eq. (6)

$$\Gamma(r_{12}) = \frac{K'}{r_{12}} \int_0^\infty I(\theta) \cdot s \cdot \sin[kr_{12}s]\, ds \tag{7}$$

$\Gamma(r_{12})$ has the property that at $r_{12} = 0$, $\xi(r_1) = \xi(r_2)$ and

$$\langle \xi(r_1)\, \xi(r_2) \rangle_{r_{12}} = \langle [\xi(r_1)]^2 \rangle_{\mathrm{av}}$$

so $\Gamma(r_{12}) = 1$. For large values of r_{12}, there will be no correlation between $\xi(r_1)$ and $\xi(r_2)$ so $\langle \xi(r_1)\, \xi(r_2) \rangle_{r_{12} \to \infty} = 0$ so $\Gamma(r_{12}) = 0$. Thus $\Gamma(r_{12})$ decreases with increasing r_{12} from unity toward zero in a manner characteristic of the order of the system. For many systems, it is found that $\Gamma(r_{12})$ may be approximated by an exponential function[8]

$$\Gamma(r_{12}) = \exp[-r_{12}/a_1] \tag{8}$$

or a Gaussian function

$$\Gamma(r_{12}) = \exp[-r_{12}^2/a_2^2] \tag{9}$$

The constants a_1 or a_2 are called " correlation distances " and are measures of the dimensions of the regions of electron density fluctuation.

A similar formalism applies to the scattering of visible light which may be used for the study of much larger heterogeneities.

In this case, the scattering power of an element is designated as $\rho(r)$ so that one has

$$I(\theta) = \left\{4\pi K_L \int_{r=0}^{\infty} \rho(r) \frac{\sin(hr)}{hr} r^2 dr\right\}^2 \tag{10}$$

$\rho(r)$ differs from the scattering power for X-rays in that X-ray scattering involves all of the electrons in atoms and is relatively unaffected by the participation of these atoms in molecules. On the other hand, light scattering involves mostly the outer or valence electrons and is quite sensitive to molecular structure.

The fluctuation in light scattering power is

$$\eta(r) = \rho(r) - \rho_0 \tag{11}$$

where ρ_0 is the average scattering power of the system. $\eta(r)$ is proportional to the refractive index fluctuation.

$$\eta(r) = C[n(r) - n_0] \tag{12}$$

where $n(r)$ is the refractive index at r and n_0 is the average refractive index.

In terms of these parameters, the equivalent expression to Eq. (2) for light scattering is[4]

$$I(\theta, \Omega) = K_L' \langle[\eta(r_1)]^2\rangle_{\text{av}} \iiint \gamma(\mathbf{r}_{12}) \cos[k(\mathbf{r}_{12} \cdot \mathbf{s})] \, r_{12}^2 \sin\alpha_{12} \, dr_{12} \, d\alpha_{12} \, d\phi_{12} \tag{13}$$

where now, the light scattering correlation function is

$$\gamma(\mathbf{r}_{12}) = \frac{\langle\eta(\mathbf{r}_1)\,\eta(\mathbf{r}_2)\rangle_{\mathbf{r}_{12}}}{\langle[\eta(\mathbf{r}_1)]^2\rangle_{\text{av}}} \tag{14}$$

If fluctuations arise from variations in the position of atomic centers, then one might expect that $\Gamma(\mathbf{r}_{12}) = \gamma(\mathbf{r}_{12})$ so that equivalent information but in different size ranges are obtained from the X-ray and light scattering experiments. $\gamma(\mathbf{r}_{12})$ may similarly be obtained from Fourier inversion of the light scattering data.

The spherically symmetrical version of Eq. (13)

$$I(\theta) = 4\pi K_L' \langle[\eta(\mathbf{r}_1)]^2\rangle_{\mathrm{av}} \int \gamma(r_{12}) \frac{\sin(hr_{12})}{hr_{12}} r_{12}^2 \, dr_{12} \tag{15}$$

has been derived by Debye and Bueche[8] and the extension to oriented systems without spherical symmetry has been made by Norris and Stein[4] and Stein and Hotta.[5] In this case, instead of a correlation function like Eq. (9) an ellipsoidal function was assumed of the type

$$\gamma(\mathbf{r}_{12}) = \exp\left[-\left(\frac{x^2}{a_2^2} + \frac{y^2}{b_2^2} + \frac{z^2}{c_2^2}\right)\right] \tag{16}$$

where a_2, b_2 and c_2 are the correlation distances in the direction of the X, Y, and Z axes which are assumed to be the principal axes of symmetry of correlation. The components of the vector $\mathbf{r}_{12}$ along these axes are x, y, and z. It is shown how a_2, b_2 and c_2 may be evaluated from a study of the dependence of scattering upon θ, Ω and ϕ (where ϕ is the tilt angle of the film sample).

Orientation Correlations

Mesophases are characteristically composed of anisotropic molecules which are arranged with correlation in their orientation. Thus, it is insufficient to specify the system in terms of only correlation functions of the atomic or molecular centers described by $\Gamma(\mathbf{r}_{12})$ or $\gamma(\mathbf{r}_{12})$. Consequently, angular dependent correlations have been introduced by Prins and Prins,[9] Peterlin,[10] Goldstein and Michaelik[11] and Stein and Wilson.[12] In its simplest form, the description requires introduction of an orientation correlation function $f(\mathbf{r}_{12})$ defined as

$$f(\mathbf{r}_{12}) = [3\langle\cos^2\theta_{12}\rangle_{\mathbf{r}_{12}} - 1]/2 \tag{17}$$

where θ_{12} is the angle between the principal polarizability axes of the scattering elements 1 and 2 specified by the unit vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ shown in Fig. 3. The average is again taken over all pairs of volume elements separated by $\mathbf{r}_{12}$. It is assumed that the polarizabilities are uniaxial with the principal values α_1 along $\mathbf{a}_i$ and $\alpha_2 = \alpha_3$ perpendicular to $\mathbf{a}_i$. The anisotropy is designated as $\delta = \alpha_1 - \alpha_2$.

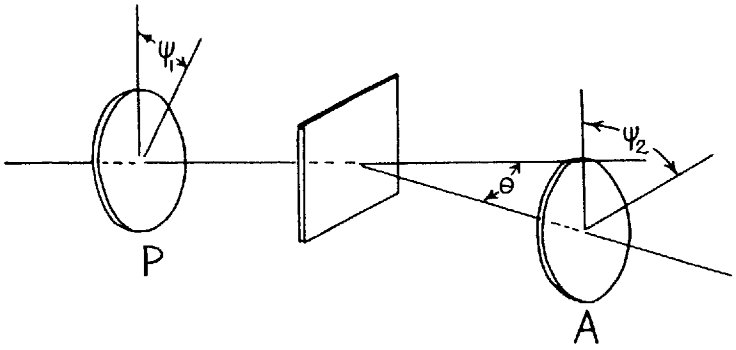

Figure 3. The angles ψ_1 and ψ_2 characterizing the orientation of the polarizer and analyzer. (From *J. Appl. Phys.* **37**, 3980 (1966).)

The function $f(\mathbf{r}_{12})$ has the property that if there is no correlation in orientation between $\mathbf{a}_1$ and $\mathbf{a}_2$ (as will be the case if they are very far apart), $\langle\cos^2\theta_{12}\rangle_{\mathbf{r}_{12}} = 1/3$ and $f(\mathbf{r}_{12}) = 0$. If the elements are very close together so that $\mathbf{r}_{12}$ approaches zero, then $\theta_{12} = 0°$, $\cos\theta_{12} = 1$ and $f(r_{12}) = 1$. Thus, as with $\gamma(\mathbf{r}_{12})$, $f(\mathbf{r}_{12})$ will be a decreasing function of $\mathbf{r}_{12}$ which may often be represented in an exponential or gaussian form.

In general, $f(\mathbf{r}_{12})$ may not only depend upon $\mathbf{r}_{12}$ but also upon the angle β between $\mathbf{a}_1$ and $\mathbf{r}_{12}$ (Fig. 2).[12-15] The special situation where $f(\mathbf{r}_{12})$ is independent of β is the case of " random orientation ", for which the regions of correlation of optic axes have approximately spherical shape with the correlation distance having no preferred value with respect to its orientation relative to the optic axis direction.

The light scattering from systems containing such orientation correlations will be enhanced because of the heterogeneity associated with such correlated regions. For the case of random correlations, Stein and Wilson[12] have shown that for the special case where the anisotropy, δ, of all scattering elements is equal, the intensity of scattering is given by

$$I_{\parallel} = K_L' \left\{ \langle[\eta(\mathbf{r}_1)]^2\rangle_{\text{av}} \int \gamma(\mathbf{r}_{12}) \cos[k(\mathbf{r}_{12} \cdot \mathbf{s})]\, d\mathbf{r}_{12} \right.$$

$$\left. + \tfrac{4}{45}\, \delta^2 \int f(\mathbf{r}_{12}) \cos[k(\mathbf{r}_{12} \cdot \mathbf{s})]\, d\mathbf{r}_{12} \right. \qquad (18)$$

and

$$I_{\perp} = K_L' \, \tfrac{1}{15}\, \delta^2 \int f(\mathbf{r}_{12}) \cos[k(\mathbf{r}_{12} \cdot \mathbf{s})]\, d\mathbf{r}_{12} \qquad (19)$$

[In these equations the volume element $d\mathbf{r}_{12}$ is an abbreviation for $(r_{12}{}^2 \sin\alpha_{12}\, dr_{12}\, d\alpha_{12}\, d\phi_{12})$ and the integral sign denotes a triple integral over r_{12}, α_{12} and ϕ_{12}.]

The symbols $I_{\parallel}$ and $I_{\perp}$ denote polarization conditions for measurement and are best seen from Fig. 3 in which ψ_1 represents the angle between the polarization direction of the polarizer (in the incident beam) and the normal to the scattering plane (in which θ is measured) while ψ_2 represents the corresponding angle for the analyzer (in the scattered light beam)[13-15]. $I_{\parallel}$ polarization designates the case where $\psi_1 = \psi_2$ while $I_{\perp}$ is that where $\psi_1 = 90° - \psi_2$.

It is seen from Eq. (18) that if the scattering elements are isotropic, $\delta^2 = 0$ and Eq. (18) reduces to Eq. (13). Also, in this case, from Eq. (19), $I_{\perp} = 0$. Thus, the scattering arising from density and orientation correlations may be distinguished from their polarization behavior. It is clear that $f(\mathbf{r}_{12})$ may be obtained by Fourier inversion of $I_{\parallel}$ while $\gamma(\mathbf{r}_{12})$ may be obtained from Fourier inversion of $I_{\parallel} - \frac{4}{3} I_{\perp}$ since

$$I_{\parallel} - \tfrac{4}{3} I_{\perp} = K_L' \langle[\eta(\mathbf{r}_1)]^2\rangle_{\text{av}} \int \gamma(\mathbf{r}_{12}) \cos[k(\mathbf{r}_{12} \cdot \mathbf{s})]\, d\mathbf{r}_{12} \qquad (20)$$

The values of $\langle[\eta(\mathbf{r}_1)]^2\rangle_{\text{av}}$ and δ^2 may be obtained from values of absolute intensities and knowledge of the constant K_L' (which may be theoretically calculated).[15-17]

Thus a description of the structure and the scattering requires at least a knowledge of two parameters $\langle[\eta(\mathbf{r}_1)]^2\rangle_{\text{av}}$ and δ^2 and of two functions $\gamma(\mathbf{r}_{12})$ and $f(\mathbf{r}_{12})$. The application of this technique to the study of the scattering by crystalline polymers indicates that the scattering may arise from both density and orientation correlations where the relative amount from each depends upon the crystallization conditions.[16–19] For liquid crystal systems, however, essentially all of the scattering arises from orientation fluctuations having correlation distances of the order of several thousands of Angstrom units.[20–22] The correlation distance is found to change continuously with temperature over a region corresponding to a given mesophase but changes discontinuously at a mesophase transition.

Non-Random Orientation Correlations[13–15]

A more striking change at mesophase transitions is in the randomness of the orientation correlations. A consequence of the random orientation correlation theory is that the scattering pattern has cylindrical symmetry about the incident beam. A means of investigating this is to measure the quantities $I_{\parallel}(\psi)$ and $I_{+}(\psi)$ as a function of ψ.

The random correlation theory predicts that at small values of θ, $I_{\parallel}$ and I_{+} should be independent of ψ. This is indeed found to be the case, for example, for the solid and smectic state of cholesteryl myristate as can be seen from the V_V scattering photograph (vertical polarizer and analyzer) of Fig. 4 indicating that correlated regions have spherical symmetry in these states.

At the transition from the smectic to the cholesteric state of cholesteryl myristate, however, there is an abrupt change in the nature of the scattering when the intensities become highly dependent dpon ψ.[21,22] Thus the cholesteric state is associated with non-randomness. Qualitative consideration of the V_V photographic scattering pattern indicates that the non-randomness is of the " disc-type " where the probability of correlation of orientation is greater for $\beta = 90°$ than for $\beta = 0°$. This gives rise to oriented regions which are extended in a direction perpendicular to that of the optic axis (Fig. 5).

For disc-like correlations, the correlation distance is greatest

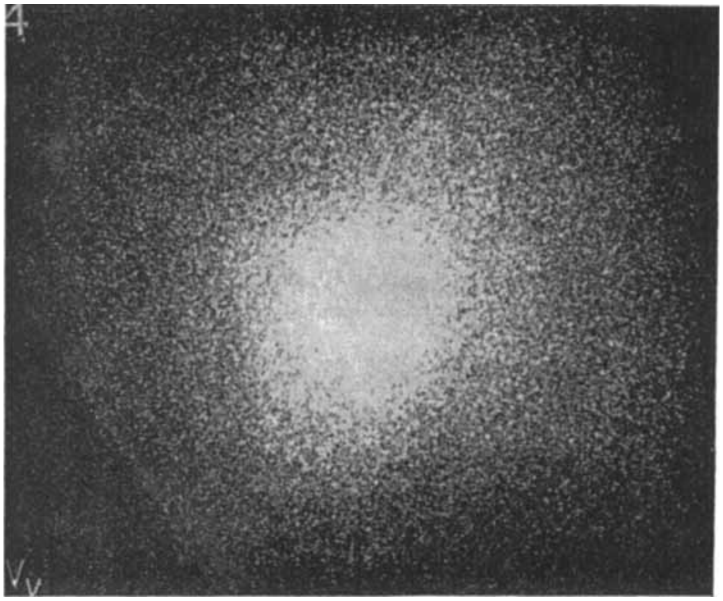

Figure 4. A V_V scattering pattern for cholesteryl myristate in the solid state. (From *J. Colloid and Interface Sci.* **27**, 3, 336 (1968).)

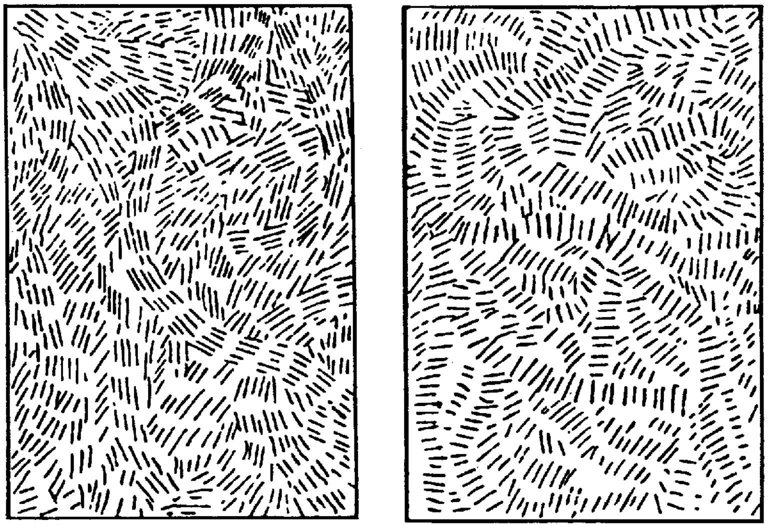
(a) (b)

Figure 5. Extended correlated regions characteristic of (*a*) rod and (*b*) disc-like randomness. (From *J. Appl. Phys.* **37**, 3980 (1966).)

in a direction perpendicular to the optic axis. The V_V scattering intensity contributed by a scattering element is proportional to $\cos^4 \theta_i$ where θ_i is the angle between its optic axis and the polarization direction (Fig. 2).[12] Thus, while the orientation directions of optic axes of the scattering elements are randomly oriented for a sample having no macroscopic orientation, those having orientations with small values of θ_i will contribute most to the scattering. Since for disc-like correlations these domains are extended mostly in a direction perpendicular to their optic axes, the effective correlation distance for the elements scattering most strongly will be greatest perpendicular to the polarization direction for V_V scattering. Since the scattering pattern is extended in a direction perpendicular to the direction of extension of the scattering object, this should result in a scattering pattern extended along the polarization direction. As seen in Fig. 6, this is the case for the cholesteric state of cholesteryl myristate. In terms of the ψ varia-

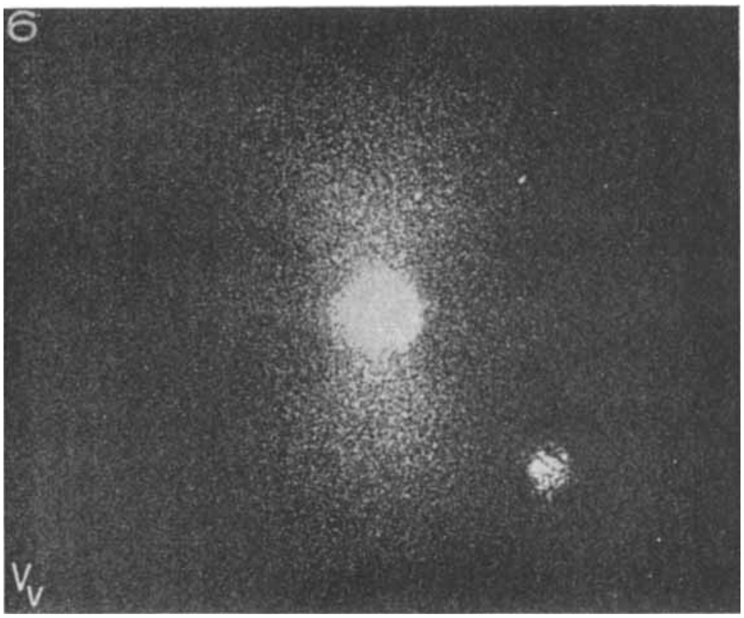

Figure 6. A V_V scattering pattern for cholesteryl myristate in the cholesteric state. (From *J. Colloid and Interface Sci.* **27**, 3, 336 (1968).)

tion, this means, as observed that $I_\parallel$ should be greatest at $\psi = 90°$. Thus this cholesteric state has disc-like order, as seems to be true of the cholesteric state of other cholesteryl esters.[22] For rod-like correlations, the $I_\parallel$ intensity should be greatest at $\psi = 0°$.[23]

Since for crossed polaroids, the intensity contribution of a scattering element depends upon $\sin^2\theta_i \cos^2\theta_i$, those elements with θ_i close to $\pm 45°$ will scatter most strongly. This gives rise to a maximum I_+ intensity at $\psi = 45°$ as is observed. This will be true for both rod and disc-like correlations, so that these cases cannot be distinguished from I_+ measurements.

The Interpolation Theory for Non-Randomness

A semi-quantitative "interpolation theory" of non-random scattering has been developed in which a parameter, ϵ, is introduced to characterize non-randomness.[13] The value of $\epsilon = 0$ corresponds to the non-random case in which the scattered intensity is independent of ψ. The value of $\epsilon = 1$ corresponds to rod-like correlations in which the optic axis angle θ_i is equal to the orientation angle α_{ij} of the vector $\mathbf{r}_{ij}$ so that $\beta = 0°$. The value of $\epsilon = -1$ designates disc-like orientation where $\beta = 90°$, whereas intermediate values of ϵ represent an interpolation between these two cases. This theory does predict that for $\epsilon \neq 0$, $I_\parallel$ and I_+ are independent upon ψ in a characteristic manner.

An observation which has been made for crystalline polymers such as polyethylene is that the extent of the variation of the scattered intensity with ψ depends upon the value of the scattering angle, θ, at which the measurements are made.[24] Since the value of θ at which scattering occurs is related to the distance r_{ij} between scattering elements, this means that degree of non-randomness depends upon the separation of the scattering elements. For example, two scattering elements which are close together may have optic axes with orientations which are correlated in a disc-like manner, while two optic axes that are more separated may have randomly correlated optic axis orientations.

In terms of the interpolation theory, they may be described by allowing the non-randomness parameter, ϵ, to be a function of $\mathbf{r}_{ij}$. In general, ϵ will depend upon $\mathbf{r}_{ij}$ in a different manner than do the correlation distances. Thus, if the r_{ij} variation of all of these quantities are representable by Gaussian functions

$$\gamma(r_{12}) = \exp\left(-\frac{r_{12}^2}{a_2^2}\right) \tag{21}$$

$$f(r_{12}) = \exp\left(-\frac{r_{12}^2}{a_3^2}\right) \tag{22}$$

$$\epsilon(r_{12}) = \exp\left(-\frac{r_{12}^2}{a_4^2}\right) \tag{23}$$

the distances a_2, a_3 and a_4 will generally be different. In this case the morphology of the system having no macroscopic orientation is describable in terms of five parameters $\langle[\eta(r_{12})]^2\rangle_{\text{av}}$, δ^2, a_2, a_3 and a_4, all of which are experimentally determinable from light scattering data.

Complications that might ensue are that the anisotropy, δ, is not constant but also fluctuates in which case δ^2 must be modified with a term involving $\langle[\Delta(r_{ij})]^2\rangle_{\text{av}}$ where $\Delta = \delta_i - \langle\delta\rangle_{\text{av}}$ and for which an additional correlation function $\psi(r_{12})$ and correlation distance, a_5, would be required to describe correlations in anisotropy.[12] For systems having macroscopic orientation, each of these correlation distances would, in general, have to be replaced by three distances, as was done, for example, in Eq. (16) for $\gamma(\mathbf{r}_{12})$.[5] Also, the value of δ^2 must be multiplied by a factor characterizing the average macroscopic orientation of the optic axes directions which may be described by one or more orientation functions.[5,16]. Thus a general description of the scattering from a system, even in terms of this simple interpolation type of non-random theory, involves a fairly large number of parameters. However, they may all be experimentally evaluated. It is physically reasonable that such a large number of parameters would be required, since one is trying to describe in terms of numbers, the details of a rather complex structure not having any simple physical form. Such a system could not be adequately characterized in terms of only a few numbers.

The Harmonic Expansion Theory of Non-Randomness

The " interpolation theory " is really only a first approximation to the description of non-randomness. Many types of non-randomness cannot be adequately described as interpolation between the rod and disc-like behavior. For one thing, the preferred orientation angle of the optic axis need not necessarily be at $\beta = 0°$ or $90°$ but could be at other angles. In fact, cases have been reported for the scattering from crystalline polymers such as polytetrafluoroethylene[23,25] and polychlorotrifluoroethylene[26] and from mesophases such as certain cholesteric states of cholesteryl propionate[22] where it has been necessary to ascribe a value close to 45° for the most probable β. Furthermore, the type of β dependence may be more complex than is describable by the simple model and the nature of this dependence may vary with r_{12}.

A more general theory of non-randomness has been proposed and worked out in detail in two dimensions.[14,15] In this case the scattering is shown to be dependent upon two two-dimensional correlation functions,

$$F_1(\beta, r_{12}) = \langle \cos 2\theta_{12} \rangle_{r_{12}, \beta} \tag{24}$$

and

$$F_2(\beta, r_{12}) = \langle \sin 2\theta_{12} \rangle_{r_{12}, \beta} \tag{25}$$

F_1 and F_2 depend upon both r_{12} and β and the averages designated as $\langle \, \rangle_{r_{12}, \beta}$ are taken over all pairs of scattering elements separated at constant values of these coordinates.

In two-dimensions, the most general way of specifying the β dependence of F_1 and F_2 is to expand in Fourier series

$$F_1 = T_0 + \sum_{n=1}^{\infty} [T_n \cos(n\beta) + Z_n \sin(n\beta)] \tag{26}$$

and

$$F_2 = S_0 + \sum_{n=1}^{\infty} [R_n \cos(n\beta) + S_n \sin(n\beta)] \tag{27}$$

In this case the Fourier coefficients are dependent upon r_{12} and are each of the nature of a correlation function. The case of random orientation correlations is that where correlations are independent of β and T_0 and S_0 are the only non-vanishing coefficients. T_0 is the two-dimensional equivalent of the previous correlation function $f(r_{12})$ and is

$$T_0(r_{12}) = \langle \cos 2\theta_{12} \rangle_{r_{12}} = 2\langle \cos^2 \theta_{12} \rangle_{r_{12}} - 1 \tag{28}$$

The S_0 term will be large if there is some preference for optic axes to be at 45° to each other so that $\langle \sin 2\theta_{12} \rangle$ is large.

At small r_{12}, optic axes will be parallel and $\theta_{12} \rightarrow 0°$. Thus $\langle \cos^2 \theta_{12} \rangle_{r \rightarrow 0} = 1$ and $T_0(r_{12}) = 1$. At large r_{12} where there is no correlation in optic axes directions, θ_{12} will be random and $\langle \cos^2 \theta_{12} \rangle_{r_{12} \rightarrow \infty} = 1/2$. Thus $T_0(r_{12}) = 0$. Thus, it is seen that like $f(r_{12})$, $T_0(r_{12})$ will decrease from one to zero over a distance dependent upon a correlation distance for orientation correlations.

It is reasonable that the average correlations for any real system will have symmetry with rotation through 180°. This means that the terms corresponding to odd values of n in Eqns. (26) and (27) will vanish.

It has been shown that the light scattering depends only upon the coefficients $(T_0 - S_0)$, $(T_2 - S_2)$, $(T_4 - S_4)$, $(Z_2 + R_2)$ and $(Z_4 + R_4)$[14]. Details of the angular dependence of correlation described by higher terms in the expansions cannot be detected by the scattering technique. Each of these coefficients will be dependent upon r_{12} in a characteristic way and serves as a correlation function. It has been suggested[14,29] that one might represent

$$(T_n - S_n) = \rho_n(r) \exp\left(-\frac{r^2}{a_n^2}\right) \tag{29}$$

$$(Z_n + R_n) = \sigma_n(r) \exp\left(-\frac{r^2}{b_n^2}\right) \tag{30}$$

where a_n and b_n are correlation distances associated with the n^{th} coefficients in the Fourier expansion and $\rho_n(r)$ and $\sigma_n(r)$ polynomial (or other simple) functions of r chosen to represent the fine details of the correlation function variations. The form of Eqns. (29) and (30) are somewhat like that of atomic wave functions.

The Z_n and R_n coefficients are zero in the case of correlations having no " handedness " where probabilities of correlation are the same at $+\beta$ and $-\beta$. Actual systems such as polytetrafluoroethylene have been found to exhibit " handedness " so that these terms cannot be neglected.

In view of this more detailed formalism, an even larger number of parameters (which are measurable) are required to specify the morphology.

At least three correlation distances, a_0, a_2 and a_4 are needed to specify the random and non-random parts and also to describe the details of the correlation. The coefficients appearing in the $\rho_n(r)$'s and $\sigma_n(r)$'s would be required. For near random correlations, the $\rho_0(r)$ coefficient would be very large as compared with $\rho_2(r)$, $\rho_4(r)$, $\sigma_2(r)$ and $\sigma_4(r)$.

The nature of the non-randomness is characterized by the magnitude and sign of the coefficients of $\rho_n(r)$ and $\sigma_n(r)$. A positive value of $\rho_n(r)$ signifies that $T_n(r)$ is larger than $S_n(r)$. In the random case, $T_0(r)$ is large and positive if θ_{12} tends to be preferentially 0° (parallel correlation) as indicated in Fig. (7a), whereas it would be large and negative for θ_{12} preferentially close to 90° (perpendicular correlation) (Fig. 7b). The term $S_0(r)$ approaches zero if θ_{12} tends toward 0° or 90° but is large if θ_{12} favors 45° being positive for $+45°$ (which we shall call positive bias correlation shown in Fig. 7c) and negative for $-45°$ (negative bias correlation in Fig. 7d). The term $S_0(r)$ would average to zero if correlation at $\theta_{12} = +45°$ and $-45°$ were equally probable at a given r_{12}. For bias correlation, $T_0(r)$ approaches zero. Thus it is apparent that a positive $\rho_0(r)$ may mean either (a) $T_0(r)$ is positive and $S_0(r)$ is small signifying parallel correlation or (b) $T_0(r)$ is small and $S_0(r)$ is negative signifying negative bias correlation. On the other hand, a negative $\rho_0(r)$ may mean either that (a) $T_0(r)$ is negative

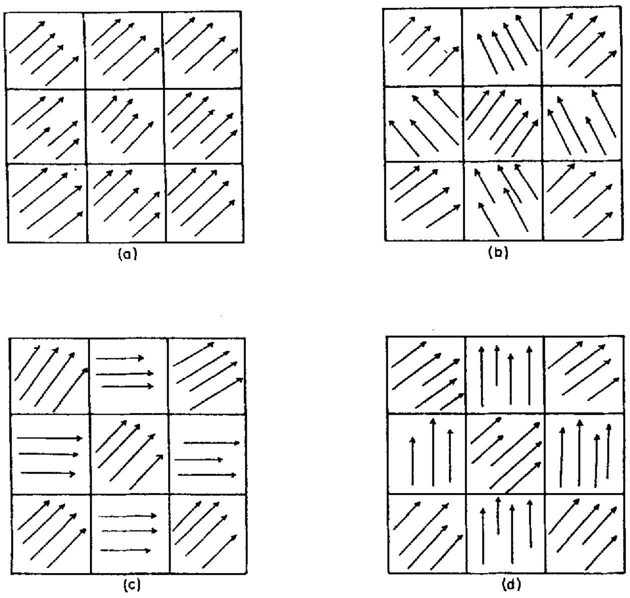

Figure 7. A lattice cell model with random orientation correlations between adjacent cells which is (*a*) parallel, (*b*) perpendicular, (*c*) positive bias, and (*d*) negative bias.

and $S_0(r)$ is small signifying perpendicular correlation or else that (*b*) $T_0(r)$ is small and $S_0(r)$ is positive signifying positive bias correlation.

As r approaches zero, correlation must approach parallel so that $T_0(r)$ should become large and positive and $S_0(r)$ should approach zero resulting in $\rho_0(r)$ becoming large and positive. Figure 8 shows how $T_0(r)$, $S_0(r)$, and $\sigma_0(r)$ would vary for the four hypothetical systems of Fig. 7. The correlation functions are seen to vary with r in a manner dependent upon the texture of the system.

For systems having some definite structure, as has been shown for two-dimensional spherulites,[14] the correlation functions may oscillate with r in a characteristic manner where $T_0(r)$ is positive for small values of r but negative for larger values. For values of r_{12} close to the radius of the spherulite, R, there is a greater

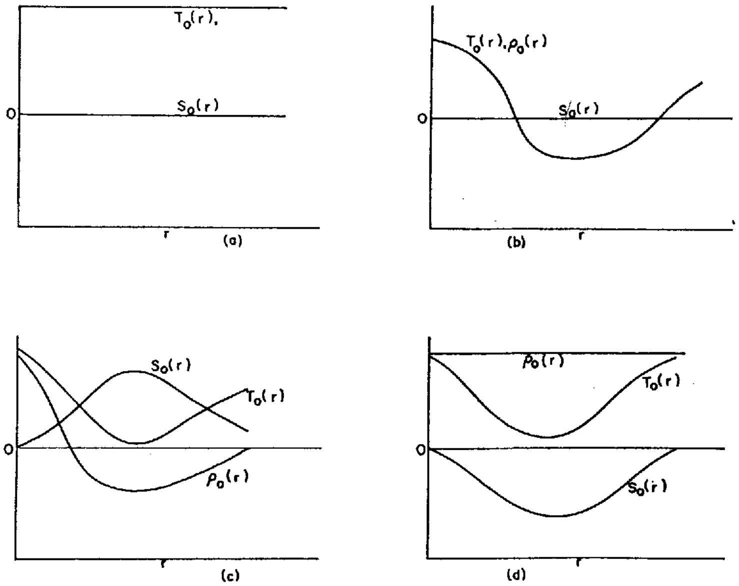

Figure 8. The correlation parameters $T_0(r)$, $S_0(r)$ and $\rho_0(r)$ corresponding to the lattice correlations of Fig. 7.

probability for perpendicular than parallel orientation so that $T_0(r)$ becomes negative.

Non-Randon Correlations in Isolated Rod-like Domains

For correlated regions have a definite shape $\rho_2(r)$, $\rho_4(r)$, $\sigma_2(r)$ and $\sigma_4(r)$ differ from zero in a manner dependent upon the shape. For rod shape correlation, the optic axes tend to be parallel only when β is close to zero (Fig. 9a). Under these conditions, $T_2(r)$ and $T_4(r)$ will both be large and positive and $S_n(r)$, $Z_n(r)$ and $R_n(r)$ will all approach zero. Thus $\rho_0(r)$, $\rho_2(r)$ and $\rho_4(r)$ will all be positive and the $\sigma_n(r)$ values will approach zero. On the other hand, for disc-like correlations where the optic axes tend to be parallel close to $\beta = 90°$ (Fig. 9b), $T_2(r)$ will be negative but $T_4(r)$ will be positive. $S_n(r)$, $Z_n(r)$ and $R_n(r)$ will again all approach zero. Thus $\rho_0(r)$ and $\rho_4(r)$ will be positive, but $\rho_2(r)$ will be negative. The $\sigma_n(r)$ terms will be small.

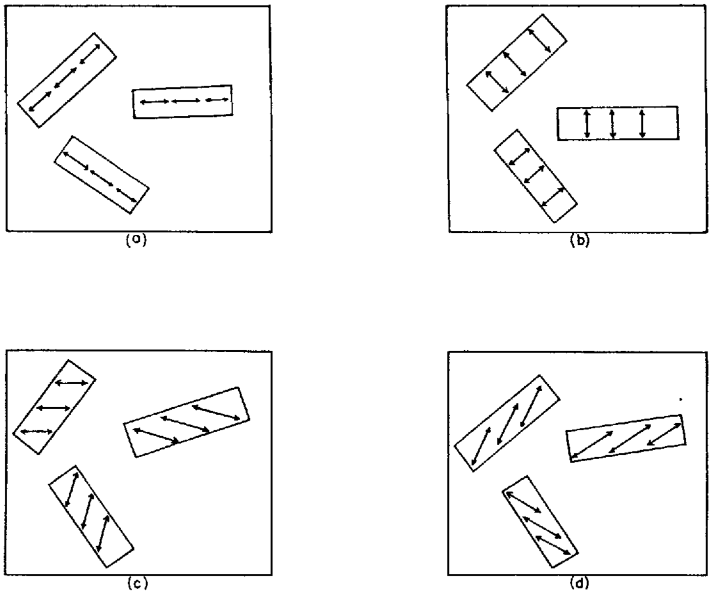

Figure 9. Some examples of non-randomness in an isolated rod-like structure with greatest probability of parallelness at (*a*) $\beta = 0°$, (*b*) $\beta = 90°$, (*c*) $\beta = +45°$, and (*d*) $\beta = -22.5°$. These rods are assumed to be randomly oriented in space and correlation between different rod-like units is not considered.

For correlations in which there are isolated rod-like aggregates in which the optic axes tend to lie at about 45° to the rod axes (Fig. 9c), $R_n(r)$ and $S_n(r)$ will still approach zero. If there is " handedness ", that is, if the probability of correlation at $\beta = +45°$ is different from the probability of correlation at $-45°$ the $Z_i(r)$ terms will not vanish. In this case $T_2(r)$ and $T_4(r)$ will be small, and $Z_2(r)$ will be positive for correlation and $\beta = +45°$ but negative for correlation at $\beta = -45°$. $Z_4(r)$ will approach zero for this case. In this case, $\rho_0(r)$ is, as usual, positive, $\rho_2(r)$ and $\rho_4(r)$ will be small, $\sigma_2(r)$ will be large but $\sigma_4(r)$ will be small. On the other hand, if correlation is greatest when β is in the vicinity of 22.5° (Fig. 9d), $Z_4(r)$ will be large so that $\sigma_4(r)$ will be large. Some of these results are summarized in Table 1. These various types of correlations are distinguishable since the correlation parameters may be determined from an analysis of the scattering data.

TABLE 1 Relationship between Types of Correlations and Correlation Parameters

Type of Correlation	Correlation Greatest for β Equal	ρ_0	ρ_2	ρ_4	σ_2	σ_4
Random	----	+ +	0	0	0	0
Rod	0°	+ +	+ +	+ +	0	0
Disc	90°	+ +	− −	+ +	0	0
Skew	+45°	+ +	0	0	+ +	0
Skew	−45°	+ +	0	0	− −	0
Skew	+22.5°	+ +	+	0	+	+ +
Skew	−22.5°	+ +	+	0	−	− −

It should be emphasized that these correlations depend upon r in a manner related to the associated correlation distances. It is possible, for example, for the correlations to be random at some r's, rod-like at others, and disc-like at still others, which leads to different ψ dependence of scattering at different values of θ.

A Lattice Model for Non-Randomness

The preceding discussion is phrased in terms of the correlations of optic axes within isolated rod- or disc-like structures. Obviously, in real systems, the structures must be space filling and may be described, for example, in terms of a lattice model as an extension of Fig. (9) which illustrates a small portion of a lattice for random orientation correlations. Such an extension for random parallel correlations in larger two-dimensional lattices has been published in which a computer has been used to generate the lattice and calculate the correlation functions.[27] Such a description may be extended to describe non-random systems. Figure 10 compares lattices for (*a*) random parallel orientation, (*b*) rod-like parallel orientation, (*c*) disc-like parallel orientation and (*d*) skew negative parallel orientation.

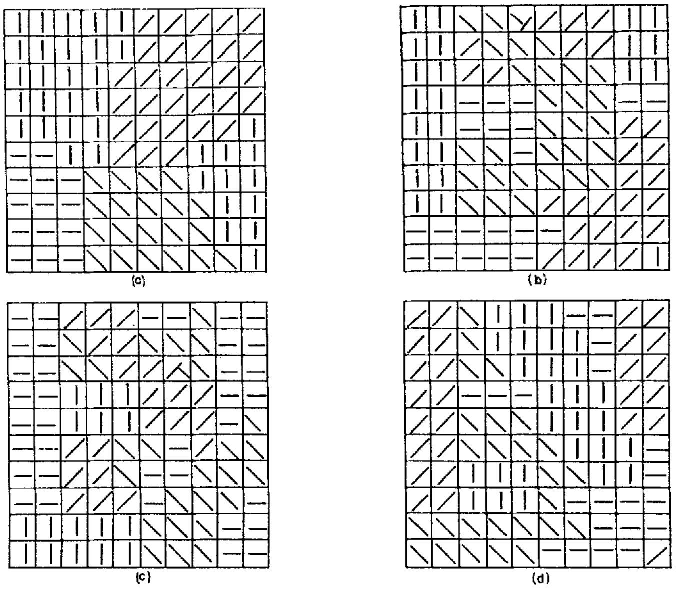

Figure 10. A two-dimensional lattice model of some types of orientation correlations in which the small lines represent optic axes directions. (*a*) parallel random orientation, (*b*) parallel rod-like orientation, (*c*) parallel disc-like orientation, and (*d*) negative skew rod-like orientation.

The associated correlation functions corresponding to those states of orientation are given in Fig. 11. In (*a*) closely spaced lattice cells have parallel orientation giving rise to domains of indefinite shape. $T_0(r)$ is large and decreases in a manner dependent upon domain size. Since there is no dependence of correlation upon β, $T_2(r)$, $T_4(r)$ and $Z_n(r)$ are small. Since there is no preferred tendency for orientation of optic axes to orient at $\theta_{12} = \pm 45°$, F_2 and consequently $S_n(r)$ and $R_n(r)$ are zero.

Figure 10b differs from 10a in that the domains are rod-like and are extended in a direction parallel to the optic axis (in the direction

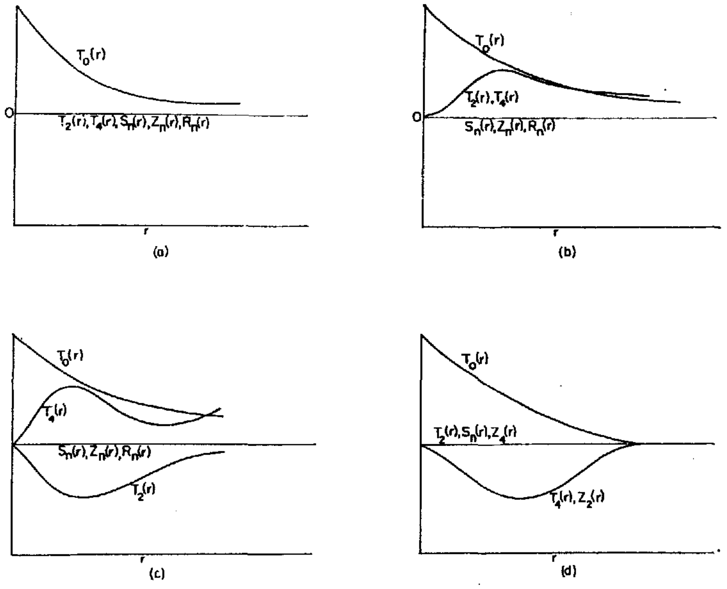

Figure 11. Correlation functions corresponding to the lattice models of Fig. 10.

of the small lines). Thus the probability of parallelness of optic axes is greater in this direction (at $\beta = 0°$) so that $T_2(r)$ and $T_4(r)$ become positive when r is greater than the domain width. For r less than this width, there is no directionality of correlation so that $T_2(r)$ and $T_4(r)$ fall to zero at small r.

In Fig. 10c, the correlations are disc-like and are extended in a direction perpendicular to the optic axes (at $\beta = 90°$). Hence $T_2(r)$ becomes negative but $T_4(r)$ is positive.

In Fig. 10d, there are 45° skew negative correlations where the probability of optic axes being parallel is greatest in a direction 45° to the optic axes ($\beta = -45°$). In this case, $T_2(r)$ is zero [since $\cos(2 \times 45°) = 0$] but $T_4(r)$ becomes negative [since $\cos(4 \times 45°)$ is negative]. It should be noted that in this case, the $S_n(r)$ and $R_n(r)$ values are still zero since there is no preference for correlation at θ_{12} of $\pm 45°$. However, $Z_2(r)$ is negative because of the handedness of the correlation at $\beta = -45°$. If correlation were greatest at + 45°, $Z_2(r)$ would be positive, and if + 45° and − 45° were equally probable, $Z_2(r) = 0$.

In the preceding cases, F_2 was zero since there was no preference for correlation at $\theta_{12} = \pm 45°$. For the model lattices of Figs. 7c and 7d, this was not so but these do not correspond to any simple physical situation. In the spherulite case with optic axes parallel (or perpendicular) to the radius at some values of r_{12}, as indicated in Fig. 12a, there is a preference for 45° orientation. As a consequence, the calculated values of $S_4(r)^{14}$ [and $S_2(r)^{28}$] are positive. For this case, there is no handedness so that the $R_n(r)$ terms are zero. A realistic case where this is not so is that shown in Fig. 12b which is the two-dimensional analog of helicoidal twist of the optic axis direction about the radius. Thus, in each successive lattice cell in the radial direction, there is a rotation of the optic axis direction of + 45° with respect to the previous case. Thus F_2 will show a maximum at a distance of about 1 radial lattice spacing. Since there is handedness in this orientation and rotation is through + 45° and not − 45°, the $Z_n(r)$ and $R_n(r)$

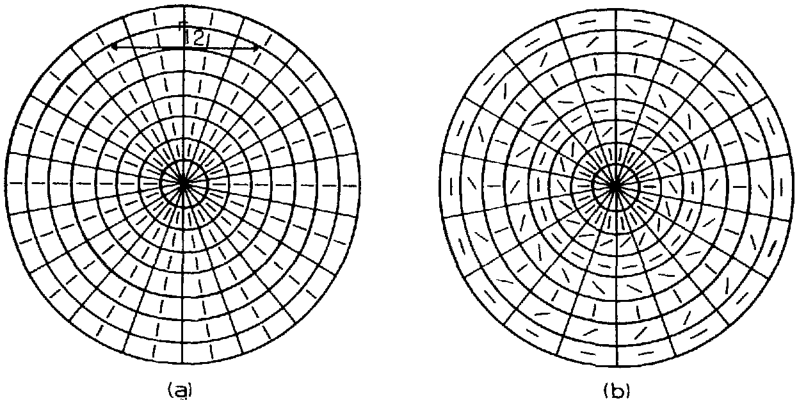

Figure 12. Orientation correlations on a two-dimensional spherulitic lattice. (*a*) The optic axis is parallel to the radius. At a distance of r_{12} there is a tendency toward orientation at $\theta_{12} = 45°$. (*b*) The optic axis rotates with respect to the radius by +45° for each radial lattice distance. This correlation exhibits " handedness ".

terms will not be zero in this case. In practice, there will be an approximately equal number of other spherulites in which there is counter-clockwise rotation rather than clockwise, but since different spherulites will generally not scatter coherently with respect to each other, cancellation of these terms between such different spherulites will not occur.

Effect of Non-Random Correlations with Macroscopic Orientation

With macroscopic orientation imposed by mechanical, electrical, or magnetic fields, all of the correlation parameters become dependent upon direction with respect to the orienting field and must be represented as vector functions. The scattering then becomes dependent upon the angle, Ω, between the orienting field and the scattering plane and intensity must be measured as a function of this angle as well as of ψ and θ. Such oriented systems are birefringent so that a correction for its effect upon the scattered intensity is essential.

Extension of Harmonic Expansion Treatment to Three-Dimensions

For mathematical simplicity, the preceding treatment is valid only where the optic axes of the scattering elements are confined to a plane perpendicular to the incident beam. While previous comparisons of the results of two and three dimensional theories indicate that there is no significant difference, a more physically realistic treatment should be developed in three-dimensions.

As has been proposed,[15] instead of expanding functions like F_2 in a Fourier series, the three-dimensional treatment requires a spherical harmonic expression. The angle between an optic axis and the vector $\mathbf{r}_{12}$ is describable in terms of two angles β and γ (Fig. 13) so that, for example,

$$\begin{aligned} F_1(\beta,\gamma) = {} & C_{0,0} + C_{1,0}\cos\beta + [C_{1,1}\,e^{i\gamma} + C_{1,-1}\,e^{-i\gamma}]\sin\beta \\ & + C_{2,0}\,[3\cos^2\beta - 1]\,[C_{2,1}\,e^{i\gamma} + C_{2,-1}\,e^{-i\gamma}]\sin\beta\cos\beta \\ & + [C_{2,2}\,e^{2i\gamma} + C_{2,-2}\,e^{-2i\gamma}]\sin^2\beta + \cdots \end{aligned} \tag{31}$$

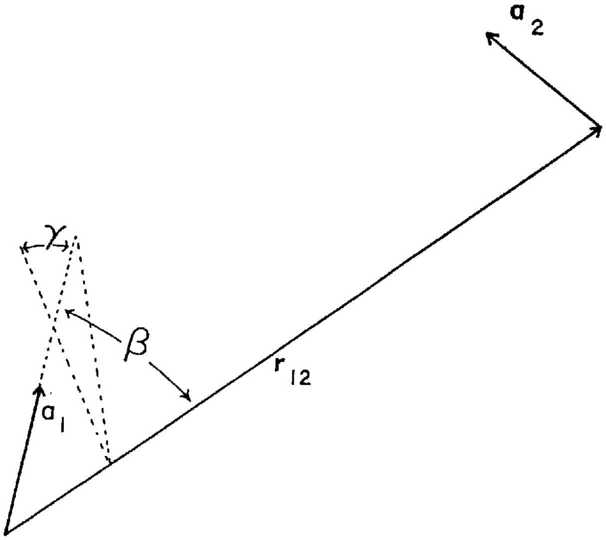

Figure 13. The angles β and γ defining the optic axis orientation in three dimensions.

For cylindrically symmetrical correlations which are independent of the azimuthal angle, γ, the coefficients $C_{l,m}$ are only non-zero when $m = 0$. (This may not be the case in biaxially oriented systems or systems with " handedness ".) For systems with correlation symmetrical upon rotation through 180°, only even values of l persist so that

$$F_1(\beta) = C_{0,0} + C_{2,0}\,[3\cos^2\beta - 1] + C_{4,0}\,[35\cos^4\beta - 30\cos^2\beta + 3] + \cdots \qquad (32)$$

The coefficients, $C_{l,0}$, are dependent upon r_{12} and now serve as correlation functions, with $C_{0,0}(r)$ characterizing the random correlations and $C_{2,0}$, $C_{4,0}$, etc., the non-random contributions. The generalization of the scattering theory involving such correlations is in progress and it is expected that the results will be formally similar to those of the two dimensional theory.

Relationship between Correlation Parameters and Mesophase Type

The classical classification of mesophase types may be reformulated in terms of the correlation parameters. Our investigations have indicated that the solid state maybe spherulitic or not depending, in the case of the cholesteryl esters, upon the type of ester and upon the crystallization conditions. The size of the spherulites, and hence the correlation distances, will depend upon the crystallization temperature.[22] Usually these distances will decrease with increasing crystallization temperature. At the solid-smectic transition, the order of the solid state appears to be preserved but there is a discrete change in correlation distance and a change in intensity of scattering. This indicates a change in the anisotropy of the scattering element, $\langle\delta^2\rangle_{av}$. At the smectic-cholesteric transition, there is a drop in scattered intensity followed by an increase characteristic of disc-like correlations. Thus, one should expect that at this temperature ρ_2 should increase negatively while ρ_4 should increase toward positive values. Cases have been reported[22] in which the scattering patterns from cholesteric phases appears characteristic of a value of β near 45° in which case one ought to find an appreciable value of σ_2. At the transition to an isotropic liquid, all of these correlation parameters should fall to small values.

While we have not yet made scattering measurements on nematic mesophases, one should expect that from their postulated structure, rod-like correlation should prevail, so that both ρ_2 and ρ_4 should have appreciable positive values.

So far, our reported light scattering measurements have been qualitative and inadequate for the quantitative characterization of mesophases. Photometric scattered intensity measurements are now being made as a function of temperature. It is hoped that these will permit the determination of the correlation parameters and distances and their temperature dependence and provide a description of mesophase behavior on a scale of detail that has not been heretofore possible.

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