1

OVERVIEW

The Rheometric Scientific Optical Analysis Module (OAM) is designed for evaluating the refractive index tensor of optically transparent or semitransparent materials. Anisotropy (non-uniformity) in a refractive index tensor provides information about the microstructure of the material. This information compliments data gained using mechanical measurements. OAM is provided as an option to the following mechanical test systems: ARES, DSR and DMTA. Adding the Optical Analysis Module to any of these turns them into an optical/mechanical test system.

1-1 SYSTEM COMPONENTS

The Optical Analysis Module (OAM) measures a material's optical response to an applied steady or step shear. Microprocessor analysis yields the following information with regard to the sample material:

- Birefringence (δn),
- Transmitted Light Intensity.
- Retardation (D)
- Orientation Angle
- Dichroism
- Shear Stress Approximation ($R2$)
- First Normal Stress Difference Approximation ($R1$)

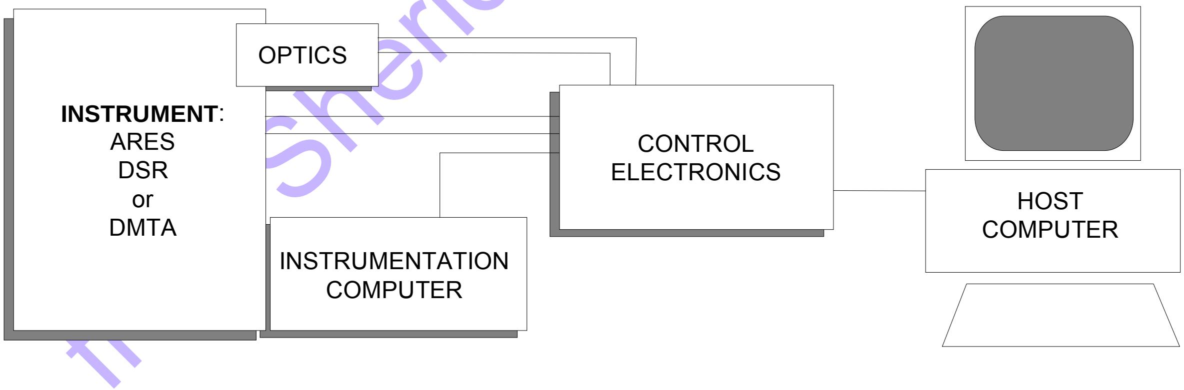


Figure 1-1 Optical Analysis Option Block Diagram

The optical analysis system is composed of the optical train (optics) and control electronics.

Optics The optics (or optical train) are contained in two parts that are mounted on the instrument on either side of the sample. The first part houses the laser diode, various optical components and the reference beam (modulation) detector. The second part contains the sample beam detector and a polarizer. The optical train is discussed in section 1-3.

Control Electronics The control electronics are contained in one electronics enclosure. It is connected to the optics by means of 2 (two) DB15 connectors: one for communication to the modulation detector and laser, the other for control of the spinner motor for the half wave plate.

Instrumentation Computer The control electronics are also connected to the instrument computer via a DB9 connector. The instrument's analog outputs for strain and synchronization are utilized by the control electronics via 2 BNC connectors.

Host Computer Communication is also provided between the host computer and the control electronics via a DB9 connector. Control of the instrument is provided with the WinRhios^{TM} software. Control of the OAM option is provided on the host computer with an additional software package.

Before entering into a detailed discussion about the operation of the optical train, an introduction to optical analysis is provided in the following section.

1-2 OPTICAL ANALYSIS: CONCEPTS AND DEFINITIONS

Optical analysis is the measurement of the interaction of light with a material. The measurement of the interaction of light with a material *while it is subject to flow* is termed **optical rheometry.** Optical rheometry measurements shed light on the state of the material's structure. The following is a discussion of optical analysis as it pertains to optical rheometry.

The Nature of Light Light behaves both as a particle and an electromagnetic wave. For the purposes of optical rheometry, only the wave nature of light will be considered here. A light wave is composed of an electric field and an orthogonal magnetic field, illustrated in Figure 1-2. The electric field has a much greater effect than the magnetic field during interactions with matter, $\varepsilon >> \beta$; therefore, the magnetic field can be ignored in this discussion.

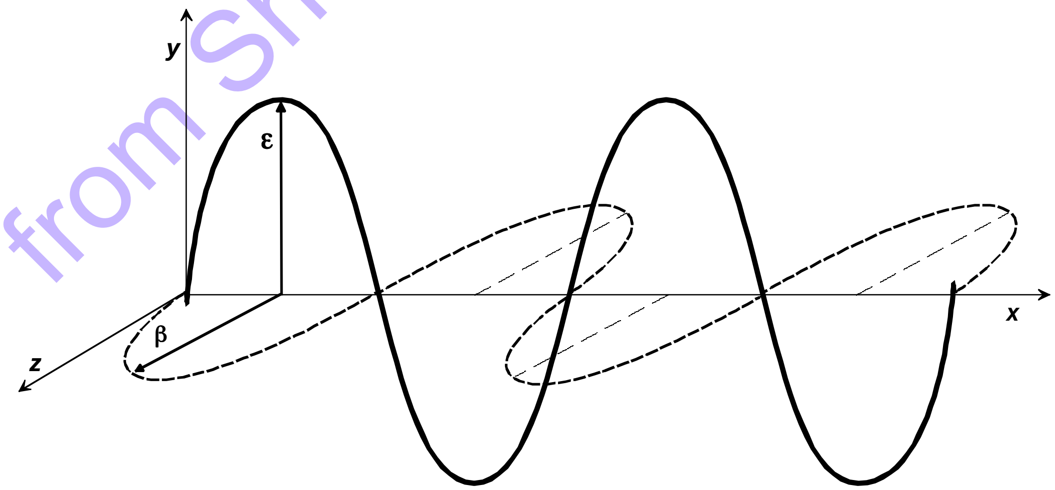


Figure 1-2 Spatial Representation of an Electromagnetic Wave

General Characteristics of Waves

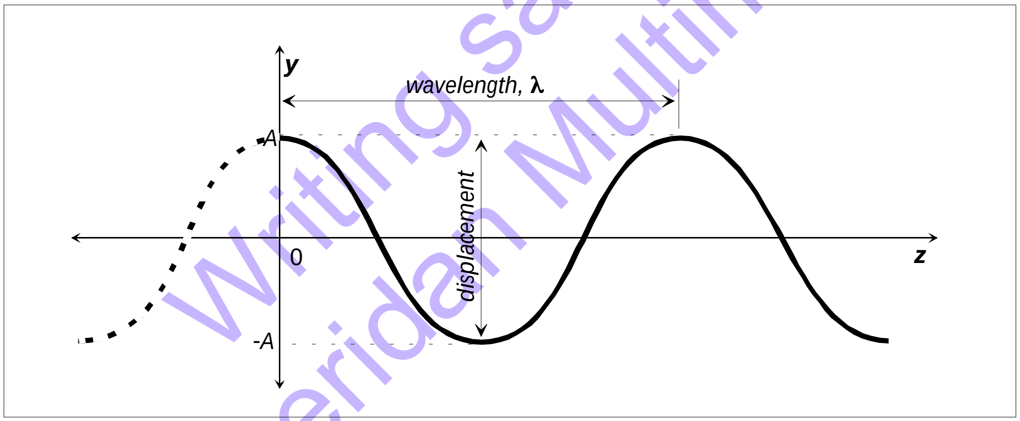
Waves have periodicity in space and time. For example, consider a vibrating stretched string. The vibrations may be thought of as the displacement of the string from a non-vibrating (rest) position (which in the figures below is indicated the *z*-axis). Periodicity in space means the displacement of the entire string at one instant in time varies periodically with position, as shown in Figure 1-3(a). Periodicity in time means the displacement of one point on the string varies periodically with time, as shown in Figure 1-3(b). A wave can be described using the following terms:

Wavelength (λ) The spatial distance between two crests, as shown in Figure 1-3(a) is the wavelength, λ.

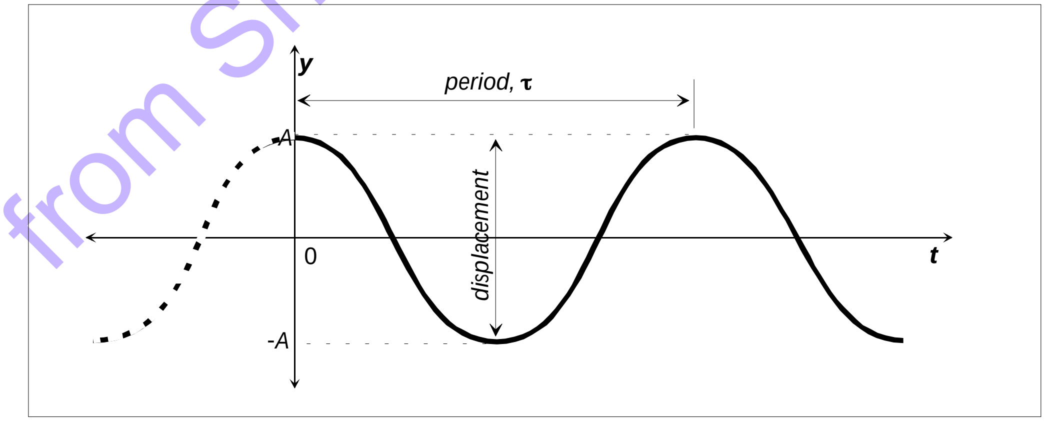
Period (τ) The length of time between two crests, as shown in Figure 1-3(b) is the period, τ.

Wave Number (n) The wave number, or spatial frequency, is the number of waves per unit length. It is defined to be the inverse of the wavelength: $n = 1/\lambda$

Frequency (ν) The frequency is the number of vibrations per unit time. It is defined to be the inverse of the period: $\nu = 1/\tau$



(a) Example of spatial periodicity in a wave



(b) Example of temporal periodicity in a wave

Figure 1-3 Components of a Wave

Mathematically, the wave shown in Figure 1-3 can be represented by the cosine of an angle, *f*, giving the displacement of any point on the axis at any instant in time:

$$x = A\cos f$$
$$= A\cos 2\pi(\nu - nz) = A\cos(kz - \omega t)$$

where x = displacement at any point z at time t
A = maximum displacement (amplitude)
$\cos f$ = phase angle
k = wave number in radians ($2\pi/\lambda$)
ω = frequency in radians ($2\pi\nu$)

Longitudinal Waves The displacement (vibration) occurs in the direction of propagation. Examples of longitudinal waves: sound waves, earthquakes.

Transverse Waves The displacement is orthogonal (at right angles) to the direction of propagation. Examples of transverse waves: light, a vibrating stretched string , waves on water.

Polarized Light Whenever the wave motion is distributed unsymmetrically in the direction of propagation, the wave is said to be polarized. Polarization can only occur with transverse waves.

Polarization Ordinary light (such as from the sun or a light bulb) is created by the emission of many light waves (or photons) from excited atoms. The electric field vibrations take place in all directions at right angles to the light propagation vector. A light wave's electric field can be represented by a complex vector that is in the plane perpendicular to the direction of wave propagation. Figure 1-4(a) illustrates the electric field vectors for light propagating perpendicular to the page (the z-axis). The complex vectors can be separated into components that are on the x and y axes (Figure 1-3(b)). The summation of all the electric field vectors in (a) are illustrated graphically in (c).

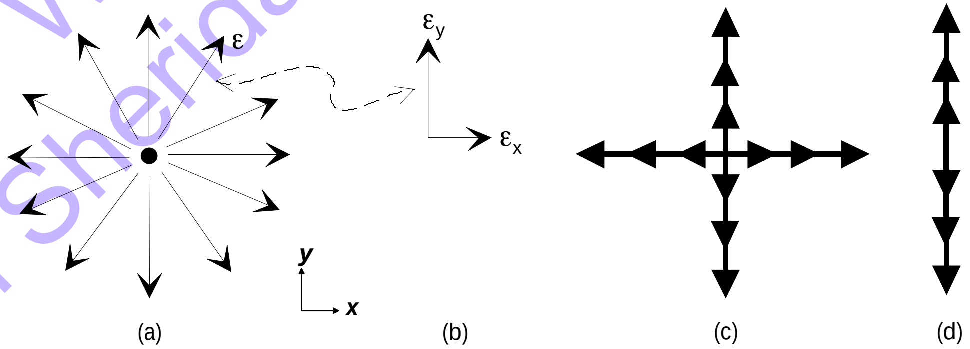


Figure 1-4 Light Expressed as Complex Vectors

The light in (c) then interacts with a *polarizer*, producing polarized light (d). The polarization process eliminates any electric field vector that is not aligned with the polarizer. Polarization can be produced by any or all of the following: selective absorption, reflection, refraction or scattering. The OAM relies on selective absorption of collimated (laser) light to generate polarized light for test purposes.

Plane Polarized Light When a collection of electromagnetic waves (such as in Figure 1-4(a)) can be described using vector components that lie in a plane, the light is said to be *plane polarized*. In Figure 1-4, the light is plane polarized in the x-y plane.

Linearly Polarized Light

Light is said to be *linearly polarized* if all of the electric field vectors lie along one axis. The light illustrated in Figure 1-2 and Figure 1-4(c) are linearly polarized.

Dichroism and Polarizers

In the very broadest sense, *dichroism* corresponds to the selective absorption of one of the two orthogonal electric field vectors comprising an incident beam of light. The earliest use of dichroic polarizers was with naturally occurring dichroic crystals such as tourmaline. Man-made dichroic devices are avaliable nowadays, the simplest of which is the wire grid polarizer.

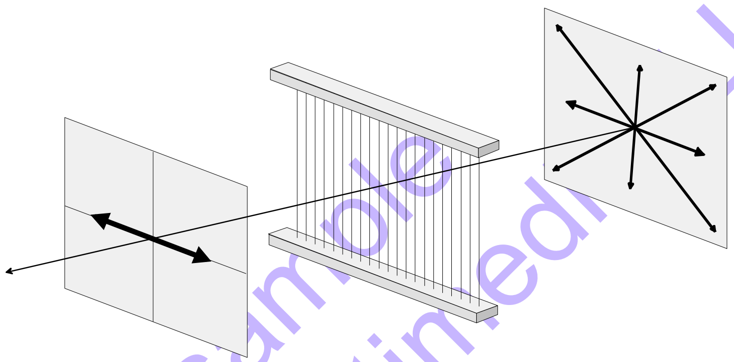


Figure 1-5 Wire-Grid Polarizer

Polarization by Selective Absorption

Figure 1-5 illustrates the polarization process using a wire-grid polarizer. The incident beam for this example is composed of microwaves. Microwaves are electromagnetic waves whose wavelengths are on the order of millimeters (visible light wavelengths are on the order of nanometers). The incident beam of unpolarized light is shown impinging on a set of closely spaced, fine conducting wires. The constituent vectors that are parallel to the wires give up energy to the wires, generating an alternating current with the electrons in the wire. In addition to joule heating, which corresponds to the removal of energy from the vertical field component, the electrons reradiate a wave which tends to further weaken the vertical field. The horizontal field, in contrast, is hardly affected by the restricted motion of electrons transverse to the wires. Therefore the transmitted beam is strongly linearly polarized perpendicular to the wires. This is analogous to what occurs when light is transmitted through a polaroid film (see note[1]).

It is interesting to note that if the light is sent through a second polarizer that is oriented 90° from the first polarizer, no light will be transmitted. This is because if the first polarizer eliminated all *y*-axis components, the second polarizer will eliminate all *x*-axis components, and there will be no more components of the light to pass through the second polarizer.

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[1] Dr. Edwin H. Land made the first commercial polarizers by heating and stretching a sheet of polyvinyl alcohol, to align its long-chain molecules, and then dyeing it with an iodine solution. The iodine, in turn, aligned itself with the polymer allowing conduction electrons from the iodine to circulate up and down the molecules as if they were microscopic wires. The resultant linear polarizer will only pass light whose **E**-field is parallel to the transmission axis. Dr. Land called this molecular analog to the wire grid **Polaroid.**

Circular Polarization

When plane polarized light interacts with certain materials (e.g. birefringent or linearly dichroic materials) or a *quarter-wave plate*, the light will experience a phase shift between its planar components. Assume an incident beam along the *z*-axis (*x*-*y* plane polarized) has had its *y*-axis component phase shifted by +90°, or ¼ of the wavelength (such a beam is illustrated in Figure 1-6(a)). The vector components of the wave ***E*** can be described mathematically as:

$$E = E_0\left[\hat{\imath}\cos(kz - \omega t) + \hat{\jmath}\sin(kz - \omega t)\right]$$

where

E = the electric field vector
E_0 = the magnitude of the electric field
i = unit vector on the *x*-axis
j = unit vector on the *y*-axis
$\omega = 2\pi\nu$ = frequency in radians
$k = 2\pi/\lambda$ = wave number in radians

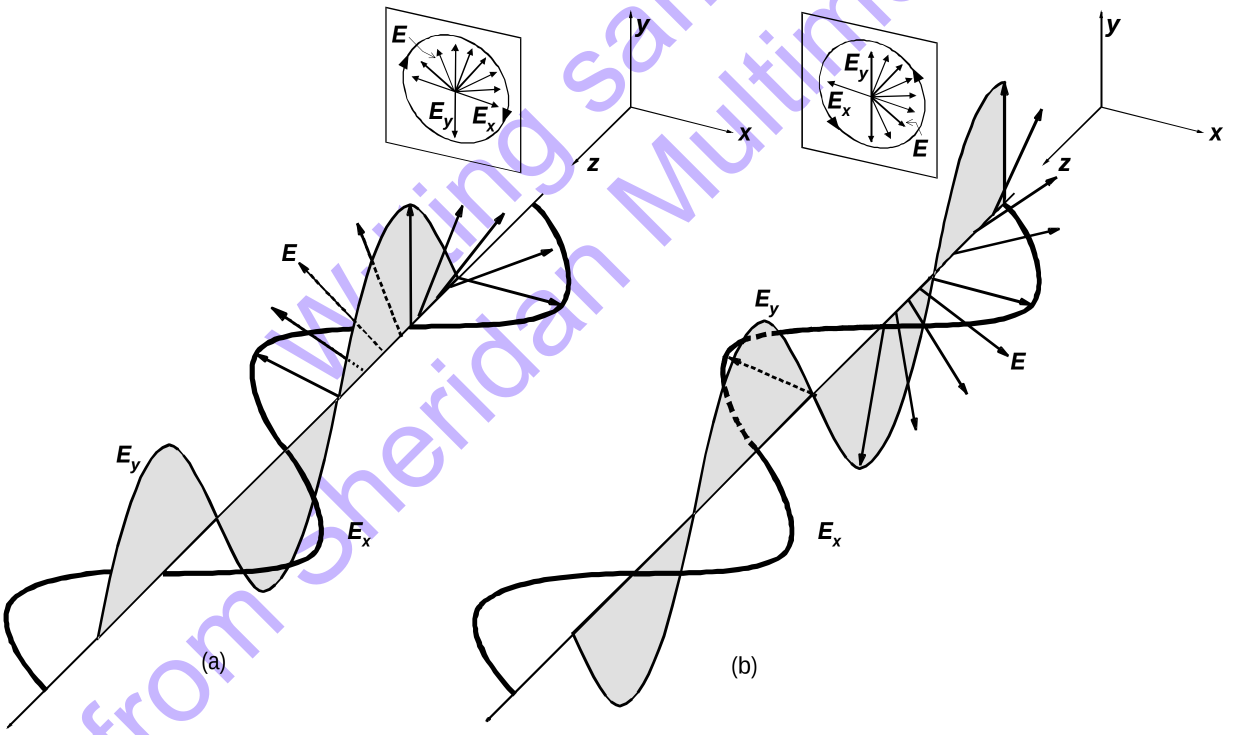

Figure 1-6 Circularly Polarized Light Waves

Right Circular Polarization

The magnitude of **E** and E_0 are constant, but the direction of **E** is a function of *z* and *t*. As shown in Figure 1-6(a), the electric field vector rotates clockwise (looking towards the source). Because the amplitude is constant, the endpoint of **E** sweeps out a circle (a circular helix, actually) with a frequency equal to that of the constituent waves. Such a field is said to be *right circularly polarized*.

Left Circular Polarization

Now let us assume that the incident beam has had its *y*-axis component phase shifted by -90° (illustrated in Figure 1-6(b)). The vector components of the wave ***E*** would then look like:

$$E = E_0\left[\hat{x}\cos(kz-\omega t)-\hat{y}\sin(kz-\omega t)\right]$$

Once again **E** has a constant magnitude, but it now rotates counterclockwise (looking toward the source). This field is *left circularly polarized*.

Elliptical Polarization

When a rotating electric field does **not** have a constant magnitude, in other words, **E** is a function of *x* and *y*, it is said to be *elliptically polarized*.

Isotropic Material

An *isotropic material* has uniform properties in all directions.

Anisotropic Material

Properties in an *anisotropic material* are not the same in all directions.

Refractive Index

When light propagates through a material, the constituent electron distribution and other charges will disturb the electric vector of the light. The bulk material property that describes the interaction is the *refractive index,* n. The refractive index is a complex quantity, with the real and imaginary parts affecting the light in specific ways.

$$n = n' + in''$$

If the electric vector of light incident on an isotropic material is given by E_0, the electric vector exiting the material is given by:

$$\mathbf{E} = E_0\, e^{i\frac{2\pi nd}{\lambda}} = E_0\, e^{i\frac{2\pi(n'+n'')d}{\lambda}} = E_0\left[\underbrace{e^{i\frac{2\pi n'd}{\lambda}}}_{\text{phase change}}\right]\left[\underbrace{e^{-\frac{2\pi n''d}{\lambda}}}_{\text{attenuation}}\right]$$

The microscopic material properties can be placed into two categories: intrinsic and form. Their effect on the refractive index is summarized in Table 1-1.

Real Part of the Refractive Index

The real part of the refractive index, n’, determines the phase change of the incident light. This affects the direction of the beam as well as the polarization of the beam, since it is derived from the electron distribution of the material. The degree of polarization will depend upon the degree of freedom experienced by electrons in the material parallel and orthogonal to the incident wave (in other words, how much the material acts like “molecular wires”).

Imaginary Part of the Refractive Index

The imaginary part of the refractive index, n”, determines the attenuation, or weakening of the incident light. The attenuation can arise from two sources, absorption and scattering. Absorption in materials that are (more or less) transparent in the visible spectrum generally occurs at very specific, discreet frequencies that correspond to excitation states of the material’s component molecules. Such response is termed *spectroscopic*, since it occurs at specific frequencies of the spectrum. Scattering occurs over the entire spectrum, and is dependent on the orientation of the molecules in the sample.

Table 1-1 Effect of Material Properties on Refractive Index

	INTRINSIC EFFECTS	FORM EFFECTS
CAUSES	• electron distribution (n') • absorption (n")	• scattering (n' and n")
DEPENDENCIES	• always present	• depends on molecular orientation • will change with deformation, temperature, etc.
EFFECT ON REFRACTIVE INDEX	• affects n' at all frequencies • affect on n" is frequency dependent	• affects n' at all frequencies • frequency of light can be selected such that n" is only dependent on scattering.

example As an example of an isotropic, unoriented, and stress-free material, consider a pane of window glass in a frame. The refractive index for glass takes the form of a single number, e.g., 1.5. If the glass is clear, the imaginary part is very small because the glass does not absorb the light, and no impurities are present to cause scattering in the glass. The previously assigned number, 1.5, is a scalar quantity, a constant throughout the sample.

Vectors Optical analysis is able to provide more detailed information about the microstructure of a material when the material is anisotropic, oriented or stressed. The refractive index is now a vector quantity, dependent on location in the material and direction of the incident light. Typically, the materials studied with optical analysis techniques have refractive indices that are not only vector quantities, but the vectors change with location and stress forces. To simplify the mathematical calculations, it is more convenient to refer to the *refractive index* ***tensor***, **n.**

Tensors A *tensor* is a mathematical notation used as a shorthand when dealing with multi-dimensional quantities. Tensors are used to describe the state of a material property at any point within a body, and can act (and be acted upon) by vectors. In rheology, the stress tensor is used to completely describe forces acting on any given point within a body.

Refractive Index Tensor In optical analysis, the *refractive index tensor* is used to calculate various material properties. It takes the same form as the vector refractive index, except now, all of the quantities are tensors:

$$\mathbf{n} = \mathbf{n'} - i\mathbf{n''}$$

where **n'** is the real part, and **n"** is the imaginary part. The light wave is a complex vector **E** having both amplitude and phase. The real part of the refractive index tensor induces a shift in the phase of the electric vector, and the imaginary part causes attenuation (weakening or reduction) of the amplitude of the vector. The magnitude of the electric vector (also called the Stokes vector) is calculated from measurements of the light intensity.

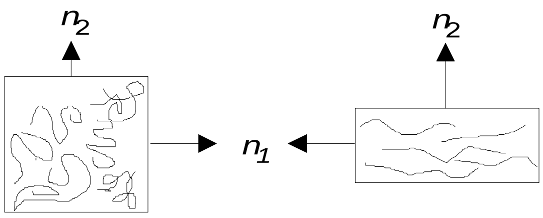

Figure 1-7 Refractive Index Components for a Polymer Sample

example Figure 1-7 illustrates what happens to a polymer sample that is physically stretched. The illustration on the left shows an undeformed polymer sample (note the coil-like polymer chains). The n1 refractive index is the same value as the n2 refractive index, but in a different direction. The vector sum of the real and imaginary parts is zero:

$$\Delta n' = n_1' - n_2' = 0$$
$$\Delta n'' = n_1'' - n_2'' = 0$$

When the polymer sample is stretched, the chains become aligned in a particular direction (as shown in the drawing at the right in Figure 1-7) and the refractive index becomes a tensor with different values in different directions:

$$\Delta \mathbf{n}' = \mathbf{n}_1' - \mathbf{n}_2' \neq 0$$
$$\Delta \mathbf{n}'' = \mathbf{n}_1'' - \mathbf{n}_2'' \neq 0$$

Differential Refractive Index If plane polarized light is incident on a material, a separate refractive index can be associated with the horizontal and vertical components of **E**: n_h and n_v, respectively. For an isotropic material, $n_v = n_h$, so no additional information can be obtained. However, if the material is anisotropic, *or can be made to be anisotropic* (by subjecting the material to stress, for instance), then $\mathbf{n_v \neq n_h}$.[2] What this means is that the vertical and horizontal components of the light wave are refracted different amounts. The difference between the refractive index of the two optic axes is described as:

$$\Delta \mathbf{n} = \mathbf{n}_v - \mathbf{n}_h = \Delta \mathbf{n}' + i\Delta \mathbf{n}''$$

Birefringence The difference in the real part of the refractive index tensor, **Δn'**, is called *birefringence*, or double refraction. Figure 1-8 illustrates what happens to the vertical and horizontal components of a light wave as it passes through a birefringent material: each component is refracted a different amount. The arrows represent *E*-field components parallel with the plane of the paper, and the circles represent components perpendicular to the plane of the paper.

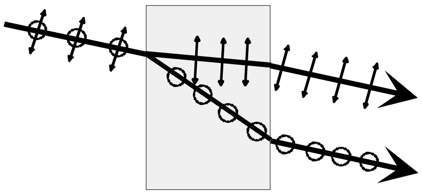

Figure 1-8 Plane Polarized Light Wave Passing Through a Birefringent (Double Refracting) Material

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[2] The separated vertical and horizontal waves emerging from a birefringent material are also referred to in the literature as the *ordinary* or *o-wave* (derived from the vector component perpendicular to the optic axis), and the *extraordinary* or *e-wave* (derived from the vector component parallel to the optic axis).

Dichroism The difference in the imaginary part of the refractive index tensor, **Δn”**, is called *dichroism.* Dichroism is related to the difference in attenuation between the two optic axes. Attenuation is caused by either scattering or absorption of the light.

Orientation Angle The orientation angles (“q” in Figure 1-9) of the principle axes of the refractive index tensor must be measured to be able to complete optical analysis calculations.

Brewster Angle Brewster’s Law states that the polarization angle, θ_P, can be determined from the formula,

$$\tan\theta_p = \frac{n_t}{n_i}$$

where n_t = index of refraction for the transmitted beam
n_i = index of refraction for the incident beam

This means when light is incident on a material at the Brewster angle, θ_P, the reflected light will be linearly polarized normal to the plane of reflection.

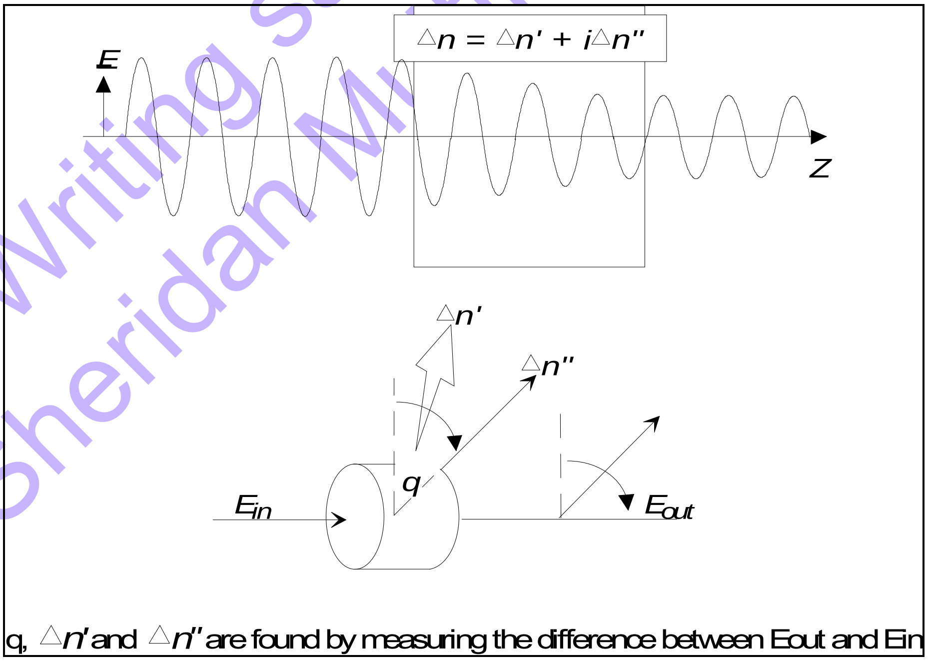


Figure 1-9 Light Propagation and Measurement Method

Propagation Effect Figure 1-9 shows the propagation effect. A light wave passes through a sample, resulting in the phase shift and attenuation of the wave. Phase shift is caused by the birefringence of the material (the real part of the refractive index tensor); attenuation is due to the dichroism of the material (the imaginary part of the tensor). The OAM measures anisotropy in both the real and imaginary tensor parts.

Intrinsic Birefringence

Measuring birefringence and dichroism provide critical information concerning the sample. A random molecular chain can be described using an end-to-end vector $\underline{R}$. The conformation of the chain is described through a distribution function, $\psi(\underline{R})$, which describes the probability that a chain will have a particular end-to-end vector. It can be shown for flexible polymer chains that are described by Gaussian statistics, the refractive index tensor is computed as

$$\underline{\underline{\mathbf{n}}} = A\int d\underline{\mathbf{R}}\,\underline{\mathbf{R}}\underline{\mathbf{R}}\Psi(\underline{\mathbf{R}}) = A(\underline{\mathbf{R}}\underline{\mathbf{R}})$$

This effect leads to intrinsic birefringence. The formula above also requires that scattering effects are insignificant. These requirements are satisfied by most transparent polymer solutions and melts. The proportionality constant, A, is related to anisotropy in the polarization of the polymer.

Stress Optical Rule

The Stress Optical Rule characterizes the stress tensor for many polymers. While it is not a general rule for all materials, it is applicable to concentrated polymers and melts. When it applies, it indicates that there is a linear relationship between shear stress and normal stress as a function of optical experimental results. For many polymers, the stress tensor is:

$$\underline{\underline{\tau}} = B(\underline{\mathbf{R}}\underline{\mathbf{R}})$$

$$\underline{\underline{\mathbf{n}}} = C\underline{\underline{\tau}} + D\underline{\underline{\mathbf{I}}}$$

where $\underline{\underline{\mathbf{n}}}$ = refractive index tensor
C = stress optical coefficient
$\underline{\underline{\tau}}$ = stress tensor
$\underline{\underline{\mathbf{I}}}$ **=** isotropic part

Particle Suspensions

When oriented, particle suspensions will also induce birefringence and dichroism. Particle orientations are described by a distribution function $\psi(\underline{\mathbf{u}})$, where $\underline{\mathbf{u}}$ is a unit vector specifying the orientation of the particle symmetry axis. It can be shown that, for a suspension of particles, the refractive index tensor can be calculated by

$$\underline{\underline{\mathbf{n}}} = B\int d\underline{\mathbf{u}}\,\underline{\mathbf{u}}\underline{\mathbf{u}}\Psi(\underline{\mathbf{u}})$$

Polymer Liquids

In polymer liquids, situations can occur that cause light to scatter, leading to form birefringence and dichroism. These effects are sensitive to the overall dimensions of the polymer chain (or aggregate of chains) instead of segmental orientation (as in intrinsic birefringence). When form effects are important, the stress optical rule (above) will fail.

1-3 OPTICAL COMPONENTS

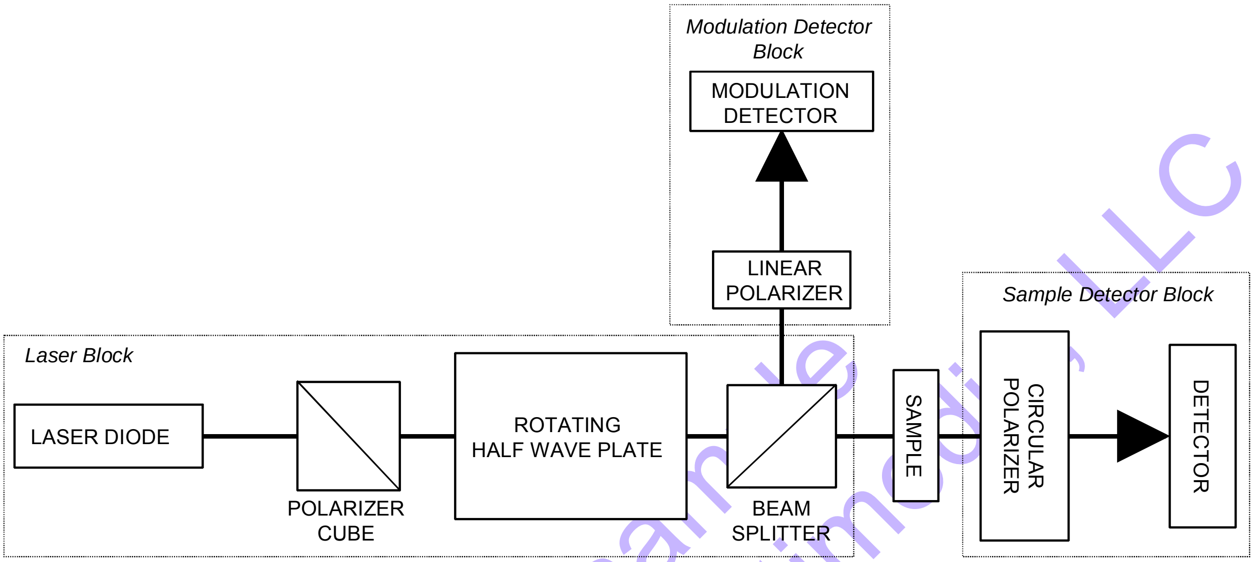


Figure 1-10 Optical Train Block Diagram

The Optical Train The components comprising the light path of the OAM taken together are referred to as the *optical train*. A block diagram of the optical train components is provided in Figure 1-10.

Briefly, collimated laser light is emitted from the laser diode and is polarized by the *polarizer cube*. The linearly polarized light is then converted to circularly polarized light by the *rotating half wave plate*. Next, the light passes through the *beam splitter* which splits it into two orthogonal beams (a reference beam and a data beam). The circularly polarized reference beam is sent through a *linear polarizer* to extract only one component for the *modulation detector* to examine. The *modulation detector* provides a phase reference for the lock-in amplifier in the control electronics.

Meanwhile, the data beam goes directly to the sample (in the case of the DMTA), or it is deflected 90° downward (for ARES and DSR products) by a pair of right-angle prisms before entering the sample. After interacting with the sample, the data beam travels through a *circular polarizer* (for birefringent test modes only. The circular polarizer is removed for dichroism tests). The resultant beam is then picked up by the *detector*, which sends information to the control electronics.

1-3.1 Laser Block

The laser block is the unit that houses the laser and the optical components indicated in Figure 1-10 and Figure 1-11. Figure 1-11 shows a cutaway view of the laser block and the locations of the optical components inside.

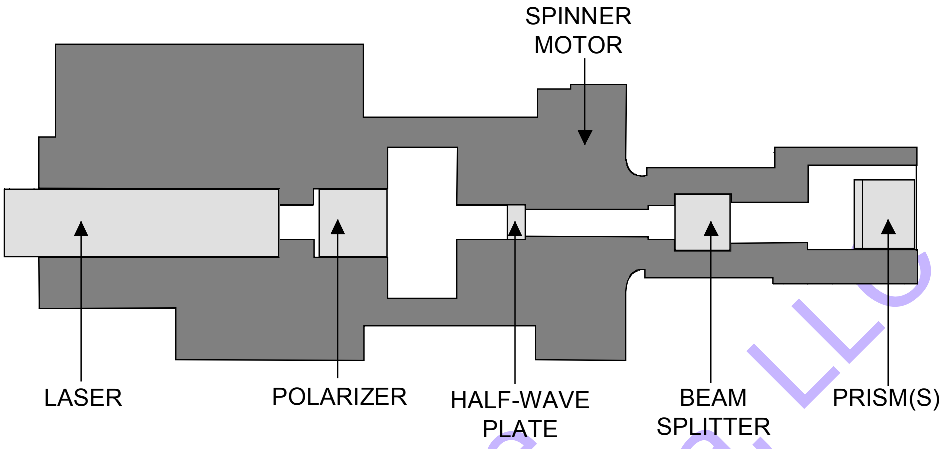
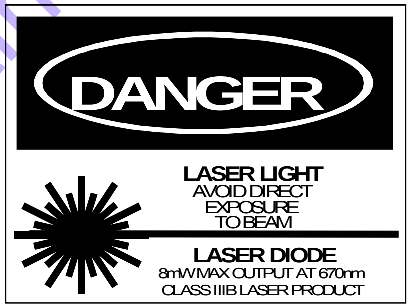


Figure 1-11 Cutaway View of the Laser Block

Laser Diode This unit provides the light for the experiment. The laser is built to emit light at a wavelength of 670nm, which is red visible. The generated laser light is polarized with a ratio of 100 to 1.

DANGER

Do not look directly into laser beam! Use care to avoid direct exposure to the beam when working with laser light; exposure can cause **permanent eye damage**.



Polarizer Cube The light then passes through a polarizer cube. This is a linear polarizer with an extinction ratio of 1000:1, providing another order of magnitude of polarization.

Spinner Motor The spinner motor provides rotation for the half wave plate The motor speed is fixed at a speed of 4 kHz.

Half Wave Plate A half wave plate rotates the polarization of the electric vector of light that is transmitted through it. A rotating half wave plate will produce an electric vector that rotates at twice the speed of the angular velocity of the half wave plate. The light transmitted from the rotating half wave plate will be circularly polarized.

The OAM utilizes a half wave plate that rotates at speed of 4kHz.

Beam Splitter (nonpolarizing) This crystal prism will split the beam into two parts of equal intensity. Half of the light will be sent to the sample and the other half will be used as a reference beam for phase information.

Prism (ARES and DSR only) There are two additional prisms held down at the exit to the laser block with a special clamp. These prisms divert the light down through the sample at 90° from the initial path of the beam.

1-3.2 Modulation Detector Block

Linear Polarizer The linear polarizer transmits only one component of the circularly polarized light to the modulation detector.

Modulation Detector The modulation detector sends phase information to the lock-in amplifier located in the control electronics.

1-3.3 Sample Detector Block

Circular Polarizer It can be shown that a circular polarizer will convert circularly polarized light into plane polarized light. The mechanism is basically the reverse of the plane-to-circular polarization process described previously. When the OAM is used for birefringence testing, the light exiting the sample will still be circularly polarized, and needs to be converted to plane polarization in order for the detected light to have relevance in subsequent signal processing. This is not the case for dichroic tests. Therefore, the circular polarizer is only used for birefringence tests, and must be removed for dichroism testing.

NOTE

For dichroism measurements, the circular polarizer must be removed from the optical train. .

Detector The detector collects the light that has passed through the sample. The information is passed on to the control electronics for analysis.