

INTRODUCTION

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The physical properties of non-crystalline solids are uniquely susceptible to study by optical techniques such as infra-red and Raman spectroscopy, reflectance and absorption measurements, and light scattering. In addition, highly refined measurements of the dependence of refractive index on pressure, density, and other parameters provide a sensitive indicator of changes in structure. Current developments in optical instrumentation and coherent optics when combined with the inherent high resolution of optical measurements, can be expected to produce improved methods of materials characterization.

In particular, Brillouin and Debye-Sears light scattering from hypersonic and ultrasonic waves can readily be applied to the study of both solid, liquid, and transition range phases of the amorphous state. The high sensitivity of the scattering process to any optical anisotropy that may be present in the substance under study offers the potential of directly observing the relaxation processes associated with longitudinal and transverse wave propagation and viscous flow.

The evolution of the elastic moduli of liquids and the formation of a shear modulus upon approach to the glass transition provide an important link in the study of glass formation. Ultrasonic attenuation measurements in liquids (Litovitz and Davis, 1965) provide a direct measure of the dispersion of compressional waves and the associated structural relaxation but are limited to the study of complex liquids with long relaxation times since the upper frequency range of these techniques in liquids is of the order of 100 MHz. Brillouin scattering from thermal excitations extends the frequency range to 10^4 MHz, where

the onset of faster relaxation processes can readily be observed. In addition, it can be expected that transverse acoustic modes can be supported by a fluid at these frequencies, a feature which appears to be verified by the recent observations of Stegeman and Stoicheff (1968). Additional features of depolarized scattering from ultrasonic waves in viscous media have been demonstrated by Kiley and Klein (1969) and by Mangla (1970) who have used Debye-Sears scattering to determine the relaxation time of viscous fluids. In this case the depolarization is attributed to flow birefringence.

Quantitative interpretation of data obtained in light scattering experiments or in refractive index measurements must ultimately rest on a theory of the optical constants which includes the magnitude and dispersion of the strain-optic coefficients. Although such a theory has been developed for cubic crystals (Maradudin and Burstein, 1967), an adequate theory is not available for amorphous systems. In the following paragraphs, after a brief review of present theories of optical constants, it will be shown that a general form of the strain-optic constants can be derived from an adaptation of the Kirkwood-Yvon theory of the dielectric constant. In this writing, the calculation is limited to include only the major features of a simple amorphous structure which contribute to the optical constants. In this context, a simple structure is taken to be an ensemble of isotropic, spherically symmetric, non-polar molecules characterized by a fixed polarizability α . Although such an assumption is a radical oversimplification of interesting non-crystalline systems, it will prove possible to infer several features which may bear on the structural evolution of more complex systems.

THEORIES OF THE OPTICAL CONSTANTS

The Lorentz-Lorenz theory of the refractive index n , given in terms of the molecular density ρ by

$$\frac{n^2-1}{n^2+2} = \frac{\alpha\rho}{3\epsilon_0} \quad (1)$$

where ϵ_0 is the permittivity of the vacuum, has been extensively used to relate optical data to changes in the state of a material. Since the only structural factor in this expression is due to the modified local field of the Lorentz cavity, which accounts for the factor n^2+2 in the denominator of the left hand side, it cannot be expected to illuminate subtle structural changes, particularly those occurring at constant density. Several authors have extended the theory of the refractive index to include the correlations of neighboring molecules using both phenomenological (Bottcher, 1952) and statistical mechanical arguments (Mazur and Jansen, 1955).

The theory of the strain-optic constants have been developed to a lesser degree. The density dependence of the refractive index can be approximated from (1) to be

$$\rho \frac{\partial n}{\partial \rho} = \frac{(n^2-1)(n^2+2)}{6n} \quad (2)$$

This expression suffers the same limitations as that for the refractive index. Furthermore, there is no possibility of developing the tensor properties of the strain-optic constants from an expression for an isotropic refractive index.

Using arguments similar to those of the Lorentz local field correction, Mueller (1955) was able to derive expressions for the anisotropy of the refractive index induced by a uniaxial strain S . From his

results,

$$(n_{11}^2 - 1)^{-1} = \frac{\epsilon_0}{\rho\alpha} - \frac{1}{3} + \frac{4}{15} S, \quad (3)$$

$$(n_1^2 - 1)^{-1} = \frac{\epsilon_0}{\rho\alpha} - \frac{1}{3} - \frac{2}{15} S, \quad (4)$$

the birefringence: for light polarized parallel and perpendicular to the strain can be derived. This derivation also provided the first valid theoretical estimate of the strain-optic constants of isotropic solids. The second and third terms on the right-hand side of these equations represent the isotropic and anisotropic local field correction.

In order to test the general validity of (3) and (4) and to extend these theories to a variety of systems which may exhibit unique structural characteristics, more general expressions for the dependence of the refractive index on focal mechanical disturbances must be developed. Progress in this direction can be readily made if it is assumed that the mechanical disturbances are infinitesimal strains which are instantaneous responses to applied uniform forces. This corresponds to the response of a system in the high-frequency limit, where the elastic moduli display solid-like behavior.

CALCULATION OF OPTICAL CONSTANTS

The refractive index and strain-optic constants of a simple amorphous system may be calculated in the high frequency limit by using the dielectric formalism of Kirkwood and Yvon as extended to optical frequencies by Fixman (1955). Assuming that the location of each polarizable center in a system of microscopic, isotropic, non-polar molecules is known and given by a hierarchy of multiparticle correlation functions, Fixman has shown that the optical dielectric constant is given by the expression

$$\begin{aligned} \overline{(\epsilon - \epsilon_0)}^{-1} &= \left[\frac{1}{\alpha\rho} - \frac{1}{3\epsilon_0} \right] \overline{\mathbf{U}} - \alpha \int_V (g_{12} - 1) \overline{\mathbf{T}}_{12} \cdot \overline{\mathbf{T}}_{21} d^3R_2 \\ &+ \alpha\rho \int (g_{123} - g_{12}g_{23}) \overline{\mathbf{T}}_{12} \cdot \overline{\mathbf{T}}_{23} d^3R_2 d^3R_3 + \dots \end{aligned} \quad (5)$$

where α is the assumed free-particle polarizability, ρ is the particle density, g_{12} , g_{123} , etc. are the two and three particle correlation functions, $\overline{\mathbf{U}}$ is the unit matrix, and $\overline{\mathbf{T}}_{ij}$ is the dipole interaction matrix given by

$$\overline{\mathbf{T}}_{ij} = \frac{1}{4\pi\epsilon_0} (\overline{\mathbf{v}}_i \overline{\mathbf{v}}_j + k_0^2 \overline{\mathbf{U}}) \frac{e^{ik_0 \hat{\mathbf{R}}_{ij}}}{\hat{\mathbf{R}}_{ij}} \quad (6)$$

where $\hat{\mathbf{R}}_{ij} = \hat{\mathbf{R}}_i - \hat{\mathbf{R}}_j$, and k_0 is the wavenumber of light in the vacuum.

Using this formalism to calculate fluctuations in the refractive index, Fixman was able to relate the molecular theory of light scattering to the phenomenological Einstein-Smoluchowski theory.

Since the expansion parameter in equation (5) is the inverse density, convergence can be expected to be slow in the range of liquid and solid densities. Nevertheless, we may gain insight into the role that molecular correlations play in structural studies of amorphous systems by

considering only terms in the expansion including the first non-vanishing correlation term and ignoring, for the moment, higher order terms. Although this may seem a drastic assumption, it is consistent with numerous studies of the role of density on refractive index, and will be adopted for the balance of this discussion.

Consider now the dependence of the dielectric constant on mechanical disturbances of the system. In particular, let us assume that the medium undergoes a sudden uniaxial strain S in the z direction. Under such circumstances it can be expected that the density and the correlation functions of a suitably truncated form of equation (5) will undergo change to correspond to this perturbation. In the absence of relaxation it follows that the new correlation function $g'_{12}(\vec{R})$ can be written in terms of the initial g_{12} by

$$g'_{12}(x, y, z) = g_{12}(x, y, z(1-S)) \quad (7)$$

Following this description, and assuming that S is infinitesimal, g_{12} can be expanded in terms of its derivative so that the strain dependence of expression (5) can be evaluated. After several changes of variable, integrating over the angular variables of the volume integral, and integrating by parts over the radius vector, the expression

$$\frac{\partial}{\partial S_z} \frac{-1}{\epsilon - \epsilon_0} = \frac{1}{\alpha\rho} \bar{U} - \frac{2}{15\epsilon_0} \bar{B} + \frac{2}{3\epsilon_0} \Gamma \left[\bar{U} - \frac{1}{5} \bar{B} \right] \quad (8)$$

is obtained. Here B is the diagonal matrix with trace zero and $B_{11} = B_{22} = 1$, $B_{33} = -2$ and Γ is the integral,

$$\Gamma = \frac{3\alpha}{4\pi\epsilon_0} \int_0^\infty g_{12}(r) \frac{dr}{r^4}, \quad (9)$$

which appears in other discussions of the refractive index.

THE OPTICAL CONSTANTS

The optical constants **of** the isotropic system may now be written in **terms** of the correlation integral. Since there are only two independent strain-optic constants in an isotropic system, it is necessary to consider only one uniaxial strain condition to obtain both. In addition, the density dependence of the refractive index is also of interest since it is this **quantity** which is readily obtained from pressure measurements and in Debye-Sears experiments.

REFRACTIVE INDEX

The refractive index obtained from direct evaluation of (5) is given most conveniently in the **form**

$$\frac{n^2+2}{n^2-1} = \frac{3\epsilon_0}{\alpha\rho} - 2 \Gamma \quad (10)$$

which can be **compared** directly to the Lorentz-Lorenz **form** of equation (1).

STRAIN-OPTIC CONSTANTS

To the extent that our approximations are valid, equation (8) can be used to predict both of the high frequency strain-optic constants of simple molecular systems. This can be done by comparing (8) to Pockel's expression for p_{11} , p_{12} (Nye, 1957) with the result that

$$p_{11} = \frac{[n^2-1]^2}{n^4} \left[\frac{\epsilon_0}{\alpha\rho} + \frac{4}{15} + \frac{14}{15} \Gamma \right], \quad (11)$$

and

$$p_{12} = \frac{[n^2-1]^2}{n^4} \left[\frac{\epsilon_0}{\alpha\rho} - \frac{2}{15} + \frac{8}{15} \Gamma \right]. \quad (12)$$

In these expressions, the fourth-rank tensor p_{ijkl} has been written in the reduced notation and the refractive index n has been substituted for the dielectric constant through the Maxwell relation $n^2 = \epsilon/\epsilon_0$.

The density dependence of the refractive index can be written in terms of (11) and (12) or derived directly from the refractive index (10) with the result

$$\rho \frac{\partial n}{\partial \rho} = \frac{(n^2-1)(n^2+2)}{6n} + \frac{2(n^2-1)^2}{3n} \Gamma. \quad (13)$$

DISCUSSION OF THE HIGH FREQUENCY OPTICAL CONSTANTS

The physical mechanisms which have a dominant effect on the optical constants of an isotropic molecular system are evident in expressions (11) and (12). The first term in the brackets of each expression accounts for the change of refractive index due to density changes accompanying a strain. The second term is the anisotropic correction to the refractive index which is attributable to the elliptical distortion of the Lorentz cavity and is the same term derived by Mueller from phenomenological arguments.

The correlation term reflects the additional polarizing effect of neighboring molecules on each other which is due to the difference between the polarization produced by a dipole spread over the volume outside of the Lorentz cavity and the polarization produced by a dipole distributed over a spherical surface centered with the Lorentz cavity.

It may be inferred that since $p_{11} \neq p_{12}$ in the high frequency limit, local optical anisotropy may be induced by either longitudinal or *transverse* hypersonic disturbances in the medium. Hence, depolarized optical scattering may be observed which is due to purely structural anisotropies which are unrelated to any anisotropies of molecular structure. This property is due to both the anisotropy of the fluctuating Lorentz cavity and to the fluctuations in the correlation term.

THE ROLE OF Γ IN THE RELAXATION OF THE OPTICAL CONSTANTS

We may now enquire what role the correlation term Γ may play in the refractive index and strain-optic constants of a substance. We will first show, from the evaluation of a class of correlation functions $g(\mathbf{r})$, that Γ will increase the Lorentz cavity contribution to **the** refractive index by 25 to 50 percent and that it may hence be expected to **have** a **measurable** effect on the observed strain-optic **constants**. We will also argue that the Γ contribution is the lowest order **term that** may be expected to exhibit relaxation and reflect structural changes in isotropic, central-force systems,

EVALUATION OF Γ

Mazur and **Jansen** have **considered** the correlation contributions to the refractive index for **Lennard-Jones** potentials. Since the behavior of Γ under changes of the internal state of a substance are of primary interest, we have **chosen** to evaluate Γ by choosing a number of correlation **functions** which typify a range of system states. Bali (1969) evaluated Γ for a number of systems for which $g(\mathbf{r})$ could be **determined**. These include three systems exhibiting a continuous $g(\mathbf{r})$, **i.e.** an uncorrelated system, and the Kirkwood-Yvon system of hard spheres in both **the Kirkwood** and Born-Green parametrization. For the sake of **comparison**, three systems with discrete distributions were also evaluated. These include the hexagonal and cubic close-packed lattices in which averages over angular variables were carried out in order to make $g(\mathbf{r})$ isotropic. The third discrete system evaluated was the random close-packed rigid sphere model of Bernal as evaluated by Scott (1962).

In figure 1, the computed values of Γ_0 have been plotted as a function of density in units of a_0^3 , where a_0 is the hard sphere diameter. Since the **polarizability** a is **unknown**, Γ_0 has been defined in terms of the classical **polarizability** $\alpha_0 = r_0^3$, where r_0 is the classical molecular radius, so that $\alpha_0 \Gamma = \alpha \Gamma_0$. It may be expected that the results of figure 1 typify a wide range of physical systems. The three discrete models correspond to the limit $T \rightarrow 0$, while the uncorrelated model **should correspond** to all systems in the limit of high temperatures. The Kirkwood-Yvon model displays the behavior of a thermodynamic system over a trajectory of temperatures (**and** hence density) at finite pressure. These results show that Γ_0 will lie between .125 and .375, indicating a correction to the Lorentz field term of between 25 to 50 percent.

It will be ~~remembered~~ **remembered** that the strain-optic properties as here derived were valid **only** in the **high** frequency limit - **i.e.** under the **assumption** that no **relaxation** of the molecular correlation would occur in response to a strain, hence a knowledge of Γ at the initial density is sufficient to **evaluate** the strain-optic constants in the high frequency limit. On ~~the~~ other hand, if the predictions of figure 1 can be taken seriously, a **qualitative** view of the **isothermal** or adiabatic **changes** in the optical constants which occur with mechanical stresses of a substance **can** be **inferred**.

In the simplest case, the value of Γ_0 is seen to be independent of density in an **uncorrelated** system. This is true in both the **isothermal** and high frequency **limits** and **implies** that no relaxation may be expected to occur in the **strain-optic** properties of the substance, regardless of the rapidity with which **mechanical** disturbances may occur. In the other extreme, the density **dependence** of Γ_0 for well defined structures such as hcp, ccp, and the **random** close-packed model at $T = 0^\circ$ is given by

$$\Gamma_0(\rho) = \rho \Gamma_0(\rho_0) / \rho_0 \quad (14)$$

This **condition** makes it possible to derive the coefficient $\rho \frac{\partial n}{\partial \rho}$ directly from the index **expression** (13). Since the above **assumption** is equivalent to solid-like **behavior**, it is not surprising that relaxation is not present in this case **either**.

It should be **noted** that an **estimate** of structural adjustments at finite temperatures **can** be **made** by evaluating Γ_0 for harmonic motion of the lattice sites. A **calculation** including **thermal** expansion would lead directly to a quantitative evaluation of the dispersion of Γ . At $T = 0^\circ$ it is clear that equation (14) is valid for these systems, while the con-

tributions at finite temperatures will be additive, increasing the value of Γ_0 at given density. It can be expected that relaxation of this additive term will accompany processes of thermal conduction.

The thermodynamic case is represented by the Kirkwood-Yvon system which illustrates the range of behavior that may be expected in the density dependence of the refractive index. Derivation of the strain-optic properties in the high frequency limit is again consistent with equation (14). This implies that the slope of the Γ_0 vs ρ curve in figure 1 is given by the line passing from the origin to the value of Γ_0 at the assumed initial density. From the figure it is clear that the dependence of Γ on density in thermodynamic equilibrium is lower than that predicted in the high frequency limit. Hence, under rapid compression from a given initial density, the system will follow the trajectory corresponding to solid-like behavior and subsequently relax (at constant density) to the equilibrium value of Γ_0 . This process is associated with the process of structural relaxation in the substance. From this point of view, the dispersion in the correlation contribution to the strain-optic constants of a substance, which we have argued is the only relaxing term in simple systems, increases at lower densities, so that its contribution to the optical properties will be considerably weaker at frequencies below the structural relaxation time. For example, in the case of the Born-Green, $\frac{\partial \Gamma}{\partial \rho} \approx .5 \frac{\partial \Gamma}{\partial \rho}$. This corresponds to the approximate relative density of Carbon Tetrachloride at standard temperature and pressure.

MOLECULAR COORDINATION

Due to the rapid decrease of the factor r^{-4} in the integrand of Γ , **this** integral is most sensitive to the density of nearest neighbors. This will be **true** even for continuous distribution functions, since an integral equivalent of **the coordination** number can be defined. **Hence**, **although** the wavelength of light is **almost** three orders of magnitude greater **than** the **interparticle** spacing, precise determination of the optical constants can be **expected** to reflect the coordination **number**. **This** suggests that the refractive index of a simple, glass forming system may indicate the **development** of increased coordination upon approaching the glass transition. A similar interpretation should be applicable to clustering of molecules in the liquid phase.

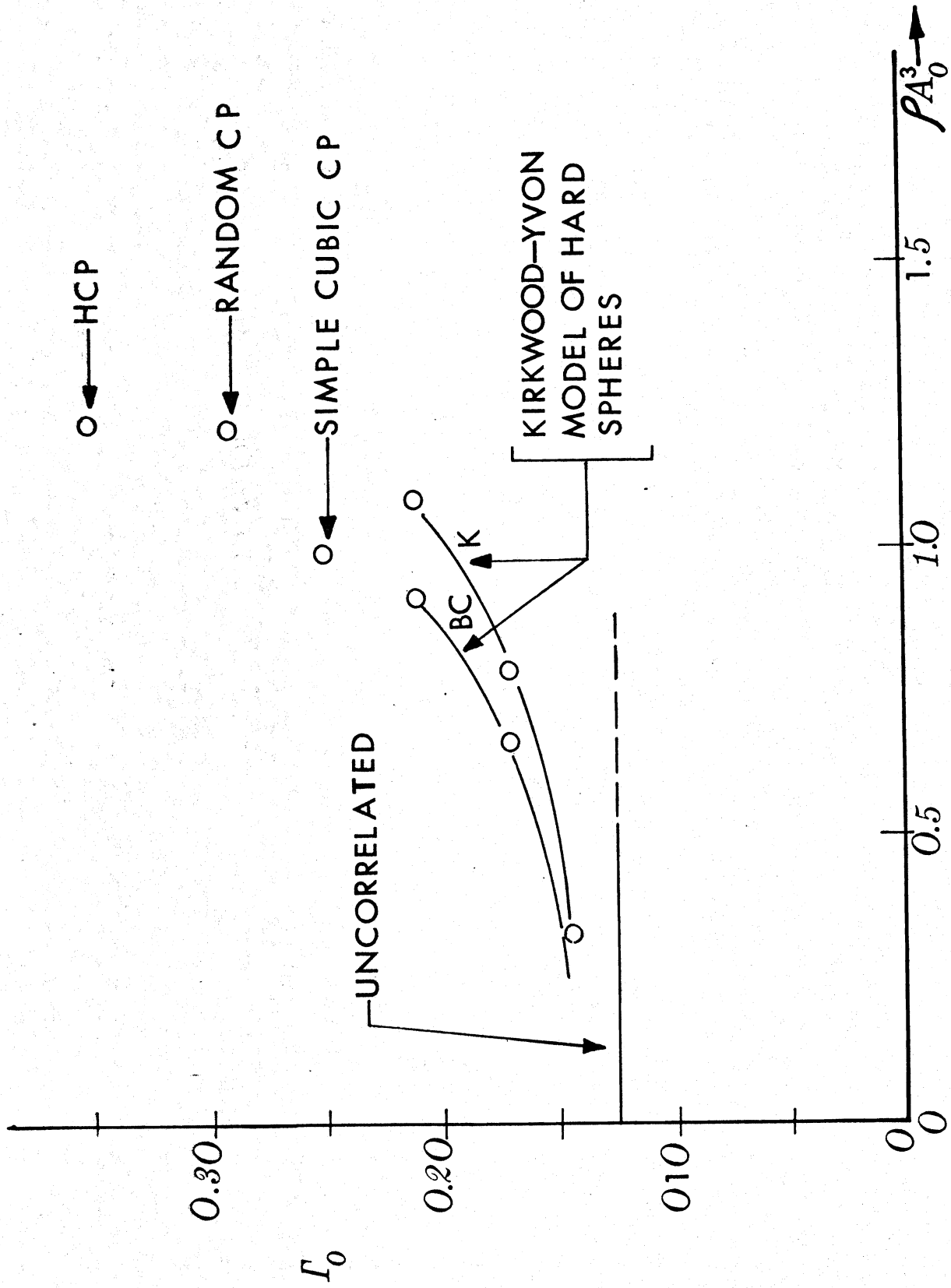
Figure 1

The dependence of the integral Γ_0 on the reduced density ρa_0^3 .

(From Bali, 1969.)

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Γ_0 VS. RELATIVE DENSITY FOR VARIOUS STRUCTURES