Notes

Orientation Induced Optical Anisotropy in Colloidal Particle Suspensions

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Received March 3, 1997

The orientation distribution of particle suspensions subject to externally imposed fields is of practical and fundamental interests as it relates to the dynamics of the suspensions since Jeffery solved the Stokes equations for the motion of a freely suspended spheroid in simple shear.[1] Particle suspensions are used in the manufacturing process in several industries for making products like paints[2] and printing inks, magnetic recording media,[3] food and pharmaceuticals, etc. Although there exist several methods for studying orientational properties of suspensions, the rheo-optical technique is advantageous over the conventional techniques because it is not only non-invasive but also capable of both spatially and temporally resolved measurements on highly dilute suspensions of Rayleigh scatters.[4-6] Even though non-spherical particles are optically anisotropic, a quiescent suspension of anisotropic colloidal particles will exhibit isotropic optical properties because Brownian motion ensures that the orientation of suspended particles becomes randomly distributed and the velocity of light through the suspension will be the same in all directions. However, if the particles in the suspension are oriented by externally imposed fields, then due to their anisotropy, the velocity of light in the suspension will be dependent on the direction relative to the particle orientation and the suspension will have different refractive indices normal and parallel to the orientation of particles. Its effective refractive index tensor is expressed as $\mathbf{n}=\mathbf{n}'-i\,\mathbf{n}''$. The real part induces a phase shift in the electric vector while the imaginary part causes attenuation of its amplitude. In general, the components of the refractive index tensor can differ and the differences in the principal eigen values of $\mathbf{n}'$ and $\mathbf{n}''$ are referred to as linear birefringence ($\Delta n'$) and dichroism ($\Delta n''$), respectively. In this note, we illustrate in a simplest procedure how a theoretical expression for the observables of the rheo-optical technique (*i.e.*, birefringence and dichroism) induced by anisotropic particle orientation is derived based on the electrostatics, and how those observables are related to particle orientation.

Theoretical Development

Change in the refractive index incurred by the presence of particles in suspension is ascribed to electromagnetic interactions of the light impinging upon the particle and the resultant scattering of the electromagnetic waves.[7,8] For a description of the scattering phenomenon by the presence of particles in terms of polarization, electric vector of scattered light, E_s is usually expressed as[7,9]

$$\mathbf{E}_S = \frac{e^{-i\mathbf{k}\cdot\mathbf{r}}}{ikr} S(\theta_k, \varphi_k)\cdot\mathbf{E}_{in} \qquad (1)$$

where · denotes the dot product of the vectors. **k** and **r** are the wave and the distance vectors, respectively. $\mathbf{S}(\theta_k, \varphi_k)$ is called the scattering amplitude tensor for the scattered light, the wave vector of which makes the angle (θ_k, φ_k) relative to the direction of the incident beam and $\mathbf{E}_{in}$ is the Jones vector of the incident light. In the above expression the time-dependent term $e^{i\omega t}$ is omitted for convenience. When a beam is incident on a slab of suspension as shown in Figure 1, the electric vector at the point O is obtained by summing the amplitude contributions of all the particles in the slab. Here, we consider particle suspension is assumed to be dilute enough such that the net scattering is obtained as linear superposition of single scattering events. Then, the electric vector at the point O can then be obtained by summing the contributions of the incidented beam and the scattered lights by all the particles in the slab of suspension and is approximated as follows[8]

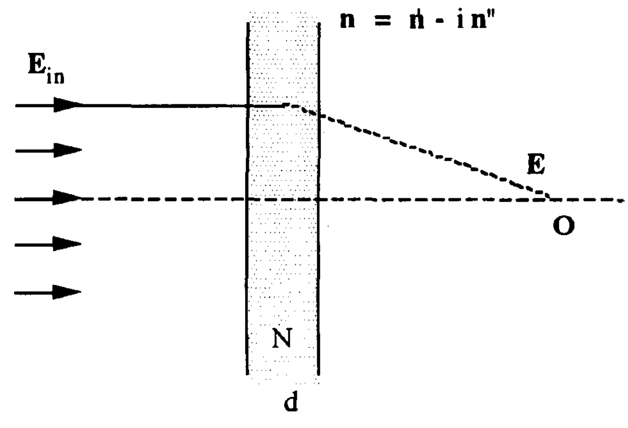

Figure 1. Scattering of light through a slab of an anisotropic particle suspension. The electric vector at the point O is obtained by summing transmitted light and all the contribution of lights scattered by the particles in the slab. The attenuation of light can also be obtained by considering the particle suspension as a homogeneous medium of refractive index **n**.

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$$\mathbf{E} = \mathbf{E}_{in} + \mathbf{E}_{s,net} = \mathbf{E}_{in} + N \int_V \mathbf{E}_s \, dV \tag{2}$$

$$\approx \left[\mathbf{I} - \frac{2\pi}{k^2} Nd \ \mathbf{S}(0) \right] \cdot \mathbf{E}_{in}$$

Here, $\mathbf{S}(0)$ is the scattering amplitude tensor at θ=0 and called the forward scattering amplitude tensor. N, d, $\mathbf{I}$ and V are the number of particles in unit suspension volume, the thickness of the slab, the identity tensor and the volume of the slab, respectively. The relationship between $\mathbf{S}(0)$ and the refractive index of the suspension in the slab can be established by considering the change in polarization of the light passing through the slab. If the refractive index of the suspension tensor in the slab is assumed homogeneous, the electric vector retarded or attenuated by the presence of suspension is expressed as

$$\mathbf{E} = [\mathbf{I} - ikd(\mathbf{n}/n_s - \mathbf{I}) + \cdots] \cdot \mathbf{E}_{in} \tag{3}$$

If the difference between the refractive indices of the suspension and the medium is small enough, the higher terms in Eq. (3) can be neglected. Then by comparing Eq. (3) with Eq. (2), we obtain the refractive index tensor as

$$\mathbf{n} = n_S \mathbf{I} - in_S \frac{2\pi N}{k^3} \mathbf{S}(0). \tag{4}$$

Here, n_s is the refractive index of the suspending medium. If we find $\mathbf{S}(0)$ in terms of particle factors, then the measured birefringence or dichroism can be correlated with the particle states using Eq. (4). The $\mathbf{S}(0)$ is, in principle, obtained by considering the scattering procedure microscopically. There are several available methods for obtaining the $\mathbf{S}(0)$.[7,9-11] Comparing to these previous methods, we obtain the $\mathbf{S}(0)$ from the electrostatics of a particle since this procedure is the simplest explanation for the scattering phenomenon.

We consider electrostatic interactions between a particle and incident light for single particle scattering events. When a beam of light impinges a particle, the particle is electrically polarized by the electric field of the light and the electric dipole induced in the particle irradiates (*i.e.*, scatters) an electromagnetic wave. In the far field region (kr>>1; this imposes Rayleigh scattering regime if the distance is replaced by the characteristic length of the particle), the electric field radiated by the dipole is expressed as[7,8]

$$\mathbf{E}_S = -\frac{e^{-ikr}}{ikr} \ \frac{ik^3}{4\pi\varepsilon_m} \mathbf{e}_k \times (\mathbf{e}_k \times \mathbf{p}) \tag{5}$$

where $\mathbf{p}$ is the electric dipole moment, and ε_m is the permittivity of the suspending medium, e_k is the unit vector in the scattering direction, and × denotes the cross product of the vectors. By introducing a polarizability tensor, α, defined as $\mathbf{p}=\varepsilon_m \alpha \cdot \mathbf{E}$, Eq. (5) can be rewritten as

$$\mathbf{E}_S = \frac{e^{-ikr}}{ikr} \ \frac{ik^3}{4\pi} (\mathbf{I} - \mathbf{e}_k \mathbf{e}_k) \cdot \alpha \cdot \mathbf{E} \tag{6}$$

Here, $(\mathbf{I}-\mathbf{e}_k\mathbf{e}_k)$ is known as the transverse projection tensor. A dot product of this tensor with any other tensor $\mathbf{A}$ gives the projection vector of the tensor $\mathbf{A}$ on the plane normal to vector $\mathbf{e}_k$. In addition, $\mathbf{E}$ in this case corresponds to the electric vector of the incident light which is in the derection $\mathbf{e}_{k0}$, where $\mathbf{e}_{k0}$ is the unit vector in the direction of the incident light.

Comparison of Eqs. (1) and (6) yields an expression for $\mathbf{S}(\theta_k, \varphi_k)$ as

$$\mathbf{S}(\theta_k, \varphi_k) = \frac{ik^3}{4\pi} (\mathbf{I} - \mathbf{e}_k \mathbf{e}_k) \cdot \alpha \cdot (\mathbf{I} - \mathbf{e}_{k_0} \mathbf{e}_{k_0}) \tag{7}$$

Here, $(\mathbf{I}-\mathbf{e}_{k0}\mathbf{e}_{k0}) \cdot \mathbf{E}_{in}=\mathbf{E}$ was used to obtain the above relationship. For a spheroidal particle, the polarizability tensor can be given in terms of particle orientation by

$$\alpha = \alpha_{\parallel} \mathbf{uu} + \alpha_{\perp} (\mathbf{I} - \mathbf{uu}) \tag{8}$$

where $\mathbf{u}$ is the unit vector along the major axis of the particle in the lab-fixed coordinates and $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the scalar polarizabilities of the particle along the major and the minor axes of revolution, respectively. $\mathbf{uu}$ is the longitudinal projection operator and gives the projection of the tensor onto a plane perpendicular to that given by $(\mathbf{I}-\mathbf{uu})$. By combining Eqs. (5), (7), and (8), one can relate the measured refractive index to the particle orientation. However, if the particle is intrinsically non-absorbing, the polarizability defined in Eq. (8) is composed of only real numbers, then $\mathbf{n}''=\mathbf{0}$, *i.e.*, dichroism does not exist. This was shown to be an incorrect interpretation.[7-9] The attenuation of light passing through a particulate medium is wholly or in part the result of scattering. Thus, the imaginary part of the refractive index of the particulate can be non zero, even if the particles are non-absorbing.[7] The misinterpretation of Eq. (7) is ascribed to unaccounted phase lags in scattered light and particle dipole induction by electric field of incident light and different levels of approximations made up to obtain Eq. (7).[8,9] Therefore, a sort of modification should be incorporated into Eq. (7). An approximate adjustment is to include the scattering contribution of non-absorbing particles. Thus, the $\mathbf{S}(0)$ can be expressed as[7,8]

$$\mathbf{S}(0) = \mathbf{X}(\mathbf{k}_0, \mathbf{k}_0) + \int_{\Omega_k} \mathbf{X}^{\dagger} \cdot \mathbf{X} d\Omega_k \tag{9}$$

with $\mathbf{X}(\mathbf{k}, \mathbf{k}_0) \equiv \mathbf{S}(\theta_k, \varphi_k)$

where Ω_k is the solid angle of the scattered light propagation direction relative to the direction of the incident beam. While the first term in the r.h.s. of Eq. (9) represents the absorption contribution, the second term is the scattering contribution.[7] Performing the integration in the r.h.s. of Eq. (9) yields a more explicit expression on the scattering amplitude tensor:

$$\mathbf{S}(0) = (\mathbf{I} - \mathbf{e}_{k_0}\mathbf{e}_{k_0}) \cdot \left[\frac{ik^3}{4\pi} \alpha + \frac{k^6}{6\pi} \alpha^{\dagger} \cdot \alpha \right] \cdot (\mathbf{I} - \mathbf{e}_{k_0}\mathbf{e}_{k_0}) \tag{10}$$

Here, k^3 and k^6 order terms are the leading terms for absorbing and non-absorbing contributions, respectively. More rigorous calculation is available in the literature[12,13] and the orders of the leading terms are shown as the same as Eq. (10). Therefore, Eq. (10) is now considered a good approximation. Inserting the polarizability tensor in Eq. (8) into Eq. (10) and comparing it with Eq. (4), we obtain

$$\mathbf{n}' = n_S \mathbf{I} + \frac{N \ n_S}{2} (\mathbf{I} - \mathbf{e}_{k_0}\mathbf{e}_{k_0}) \cdot [B_{\parallel} \mathbf{uu} + B_{\perp} (\mathbf{I} - \mathbf{uu})] \cdot (\mathbf{I} - \mathbf{e}_{k_0}\mathbf{e}_{k_0}) \tag{11a}$$

$$\mathbf{n}'' = \frac{N \ n_S}{2} (\mathbf{I} - \mathbf{e}_{k_0}\mathbf{e}_{k_0}) \cdot [A_{\parallel} \mathbf{uu} + A_{\perp} (\mathbf{I} - \mathbf{uu})] \cdot (\mathbf{I} - \mathbf{e}_{k_0}\mathbf{e}_{k_0}) \tag{11b}$$

with

$$i\,\alpha_{\parallel} + \frac{2k^3}{3}\alpha_{\parallel}^{*}\alpha_{\parallel} = A_{\parallel} + i\,B_{\parallel}$$

$$i\,\alpha_{\perp} + \frac{2k^3}{3}\alpha_{\perp}^{*}\alpha_{\perp} = A_{\perp} + i\,B_{\perp}$$

where $A_{\parallel}$, $B_{\parallel}$ and $A_{\perp}$, $B_{\perp}$ are real numbers, and superscript * denotes the complex conjugate. Eqs. (11a) and (11b) relate the particle orientation to birefringence and dichroism regardless of the presence of absorbing/non-absorbing components in particle polarizability. Here, $(\mathbf{I}-\mathbf{e}_{k_0}\mathbf{e}_{k_0})$ tensor is a transverse projection operator and thus $(\mathbf{I}-\mathbf{e}_{k_0}\mathbf{e}_{k_0})\cdot\mathbf{A}\cdot(\mathbf{I}-\mathbf{e}_{k_0}\mathbf{e}_{k_0})$ represents the projection of a tensor $\mathbf{A}$ on the plane normal to the direction of $\mathbf{e}_{k_0}$. In other words, Eqs. (11a) and (11b) imply that the refractive index tensor is proportional to the particle orientation projected upon the plane normal to the light propagation direction. Further expansion of Eqs. (11a) and (11b) give explicit characteristics of the particle orientation in terms of birefringence and dichroism. If we take $\mathbf{e}_{k_0}$ as the z-axis in the Cartesian coordinate, then the refractive index tensor encompasses the **x-y** plane. Eigen values of the tensor can be easily found and the difference between the eigen values (*i.e.*, birefringence and dichroism) can then be obtained by

$$\langle\Delta n\rangle = M\,[(\langle u_x u_x\rangle - \langle u_y u_y\rangle)^2 + 4\langle u_x u_y\rangle^2]^{1/2} \qquad (12)$$

where

for birefringence ($\Delta n \Rightarrow \Delta'$), $M = \dfrac{Nn_S(B_{\parallel} - B_{\perp})}{2}$

for dichroism ($\Delta n \Rightarrow \Delta''$), $M = \dfrac{Nn_S(A_{\parallel} - A_{\perp})}{2}$

Here u_i (i=x, y) is the i-axial component of the particle orientation vector, **u**. The angle bracket denotes an ensemble average of all particle orientations. This is used since the experimentally measured quantity is the average orientation of the particles in the suspension (*i.e.* $\langle A(u)\rangle = \int_u A(u)\,F(u)\,du$, where F(u) is the orientation distribution funtion for particle orientation, **u**).

The rheo-optical experiments to investigate the dispersion state of colloidal suspensions using the theoretical results in this study can be built on the foundations of polarimetry. Polarimetry experiments are those where the canges in the polarization state of light emanating from a sample are analyzed. When polarized light interacts with a material having an anisotropic refractive index **n**, the polarization state of light emitted from the sample will generally be altered. Changes in polarization through optical elements are described by incorporating the corrsponding Jones calculus as follows:[14]

$$\mathbf{E}_{out} = [\mathbf{J}(\mathbf{n})]\cdot\mathbf{E}_{in} \qquad (13)$$

where **[J]** is the Jones matrix for the particular sample and is a function of the refractive index of the sample. For a generalized anisotropic material, the Jones matrix of the material takes the following form:

$$[\mathbf{J}(\mathbf{n})] = e^{N} \qquad (14)$$

where, **N** is the Jones matrix for an infinitesimal layer of the material. In the particle suspensions in this study, optical anisotropy originates from the orientation of optically anisotropic particles. Consequently, the axes of the birefringence and dichroism are considered to coincide since they will be parallel to the axis of particle orientation. When the two axes coincide, Eq. (14) is simplified to[14]

$$[\mathbf{J}(\mathbf{n})] = \mathbf{R}(-\chi)\begin{bmatrix} e^{-A_x + i\phi_x} & 0 \\ 0 & e^{-A_y + i\phi_y} \end{bmatrix}\mathbf{R}(\chi)$$
$$= e^{-A_x + i\phi_x}\,\mathbf{R}(-\chi)\begin{bmatrix} 1 & 0 \\ 0 & e^{LD' + iLB'} \end{bmatrix}\mathbf{R}(\chi)$$

where **R** is the rotation matrix for the rheo-optic elements, and A_i and ϕ_i are the absorbance and the absolute phase retardation along i-axis of the principal refractive index, respectively. Furthermore, $LD' = -(A_y - A_x)$ and $LB' = \phi_y - \phi_x$ are the quantities which are closely related to the linear dichroism and the linear birefringence, respectively. Macroscopically, the differences in phase retardation and absorption between the principal axes are related the differences in the optical path length through the following;[15]

$$LB' = \frac{2\pi}{\lambda}d\,\Delta n' \quad \text{and} \quad LD' = \frac{2\pi}{\lambda}d\,\Delta n'' \qquad (16)$$

where λ is the wave length of the light impinging upon the sample and d is the length of the medium through which the light travels. Both $\Delta n'$, $\Delta n''$ can be, thereby, measured from the experiment.

In the polarimetry characterization system, polarization of an incident beam is first adjusted by passing it through a group of optical elements (A), which can be any combination of optical elements such as a polarizer, a photoelastic modulator and a quarter wave plate, etc. Subsequently, the light impinges upon a sample (F). The light coming from the sample is modified by passing another group of optical elements (B) to generate a desirable condition for analysis. Both dichroism and birefringence can be determined through the light intensity measurement in polarization modulation technique. Dichroism is obtained from the arrangement of A and F, however birefringence is obtained from the arrangement of A, F and B.

Recently, there have been many experimental observations of the rheo-optical property on magnetic particle suspensions. Zhang *et al.*[16] studied how a theoretical model of light scattering from a ferrofluid in a magnetic field is established on the basis of classical dipole element oscillation theory. We[17-20] also have extensively investigated the orientation distribution of magnetic particle suspensions (rod-like γ-Fe_2O_3 or CrO_2 and plate-like Ba-Ferrite) subjected to external magnetic and by hydrodynamic fields using the polarization modulation dichroism measurement technique. A simple scaling model for dichroism and birefringence in magnetic fluids is also proposed by Shobaki *et al.*[21] and the isothermal dichroism and birefringence are superimposed into a single function.

Conclusions

If particle suspension is subjected to an axisymmetric field, the particle orientation would be independent of φ in

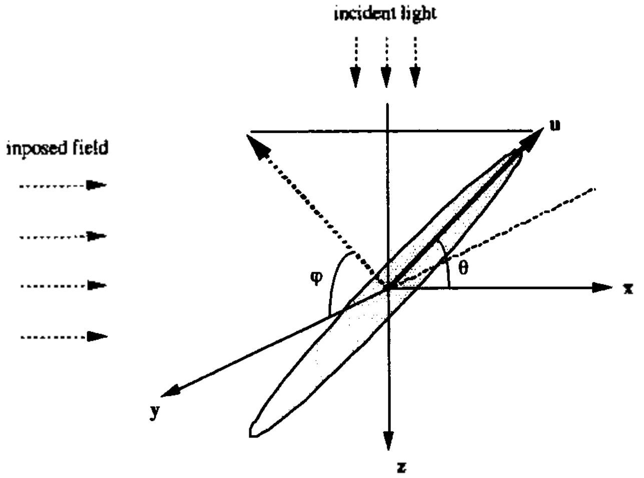

Figure 2. Coordinate system adopted for a particle orientation. The direction of light propagation is normal to the imposed field direction. Angle of the major axis of the particle relative to the imposed field direction is incorporated into the order parameter.

the coordinate system illustrated in Figure 2. Then it can be easily shown that Eqs. (11a) and (11b) for birefringence and dichroism are directly related to the ensemble average of the second Legendre polynomial, P_2.

$$\frac{<\Delta n>}{<\Delta n>_{max}} = \frac{S}{S_\infty} \tag{17}$$

with $S=<P_2(\cos\theta)>=<(3\cos^2\theta-1)>/2$

Here, S is referred to as the order parameter and S_∞ is the quantity of the order parameter obtained at perfect particle orientation. $<\Delta n>_{max}=M\ S_\infty$ is the maximum birefringence or dichroism from Eq. (12), occurring at perfect particle alignment and is a constant dependent upon parameters such as the particle concentration, intrinsic optical properties of the particles and the suspending medium, and characteristics of the light beam adopted for test, etc. According to Eq. (17), $(\Delta n)/(\Delta n)_{max}$ is a range from 0 (random orientation) to 1 (perfect alignment), regardless of particle shape. Observed orientation characteristics of differently shaped particles can be directly compared in terms of the quantity.

Finally, it is concluded that a theoretical derivation for both birefringence and dichroism through Eqs. (11) and (12) obtained in this note based on the electrostatics is much simpler than those obtained from both Ráyleigh-Debye-Gans approximations[13] and integral expressions[12].

Acknowledgment. One of the authors (H. J. Choi) wishes to acknowledge the partial financial support of the Research Fund for Advanced Materials (1995) through Korean Ministry of Education.

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