CHAPTER IV

APPLICATION OF THEORY
CHAPTER IV

APPLICATION OF THEORY

(A) DEVELOPMENT OF METHOD

(B) DETERMINATION OF MAGNETIC PROPERTIES

(C) ANISOTROPY AND OPTICAL ANISOTROPY

(D) EXPRESSIONS OF OPTICAL ANISOTROPY FOR

   (i) Absorbing, isotropic, non-spherical particles
   (ii) Absorbing, anisotropic spheres
   (iii) Absorbing, anisotropic, anisometric particles

REFERENCES
The theory described above, and the expressions discussed before provide a very useful technique for determining several important parameters pertaining to the particles dispersed in a system. Amongst these are:

(i) Anisometry
(ii) Magnetic anisotropy and the permanent magnetic moment
(iii) Average size and size distribution

Of these, mainly (i), (ii) are considered. Magneto-optical effects in dispersions of graphite have been used to determine the average size and size distribution (Ref. 1). In the same paper they have also considered the anisometry of the graphite particles.

It is even possible that, from a careful study of the wavelength-dependence of the birefringence and dichroism in a magnetic field, one can get useful information regarding the optical anisotropy of the dispersed particles.

In order to see how the expressions given earlier (p. 82) can best be utilized, one notes that they can be
written in a following general form, which holds good in all the four particular cases.

\[(Q_L - Q_R) = (Q_L - Q_R)_\infty \cdot (3 \phi(h) - 1) \ldots (1)\]

\[\delta = (\delta)_\infty \cdot (3 \phi(h) - 1)\]

Also,

\[h = A \cdot h \ldots (2)\]

The particular form assumed by \(\phi(h)\) in the individual cases, appropriate expression for \(A\) and other important particulars are tabulated in the table no. 3 p.83.

From equations (1) and (2), one gets:

\[\log (Q_L - Q_R) = \log (Q_L - Q_R)_\infty + \log (3 \phi(h) - 1)\]

\[\log \delta = \log (\delta)_\infty + \log (3 \phi(h) - 1) \ldots (3)\]

\[\log h = \log A + \log h \ldots (4)\]

The experimental results can be plotted graphically with \(\log h\) along abscissa and \(\log (Q_L - Q_R)\) along ordinate. Similarly the theoretical expression for \(\phi(h)\) can also be plotted with \(\log h\) along \(X\)-axis and \(\log (3 \phi(h) - 1)\) along \(Y\)-axis (i.e., ordinate). Equations (1) and (2) show that if the function \(\phi(h)\) is correctly chosen, then the above two graphs can exactly be superposed on one another, with an appropriate shift of the origin; i.e., if the origin of the
theoretical graph of $\log (3\phi(h) - 1)$ vs. $\log h$ is selected at a point $X = \log \phi$; $Y = \log (Q_L - Q_R)$ on the experimental graph, then two will coincide.

This technique immediately provides us with the following information:

(i) The form of $\phi(h)$ that is required to be selected for the closest agreement with the experimental data reveals the nature of the torque.

(ii) The shift of origin of theoretical graph along the abscissa to achieve the superposition gives the constant $a$. The constant $a$ is related to the magnetic anisotropy or polar moment and the particle size.

(iii) The shift $Y$ along the ordinate leads to the value of $(Q_L - Q_R)\infty$ or $(\delta)\infty$. This parameter can lead to the determination of anisometry as shown later.

It will not be out of place to state here that in the case of particles with anisotropic magnetic susceptibility, the saturation values in magneto-optical effects i.e., $(Q_L - Q_R)\infty$ and $(\delta)\infty$ can also be determined by plotting $\Theta$ vs. $1/h^2$; and $\delta$ vs. $1/h^2$; and reading the intercept on the ordinate. This method is based upon the fact that the limiting expressions for the function $\phi(h)$ are:

(i) $h < 1: N(h) \to 1/3(1 - 4h^2/15); P(h) \to 1/3(1 + 4h^2/15)$

(ii) $h > 1: N(h) \to 1/2h^2; P(h) \to (1 - 1/h^2)$
Thus, the magneto-optical effects will be proportional to $H^2$ at low fields and $1/H^2$ at high fields. However, in the case of $L(h)$ function, it is not so, since:

(i) $h \gg 1 : L(h) \rightarrow (1 - 2/h + 2/h^2)$

(ii) $h \ll 1 : L(h) \rightarrow 1/3(1 + 2h^2/15)$

Thus, at high fields the effects are not proportional to $1/H^2$ and therefore, this method is not applicable. This graphical method is particularly more useful when the particles show large absorption variation as in the case of molybdenite (Ref. 2) dispersions. In the present work, almost all colloids studied show the presence of dipolar moment and, therefore, this method is not used.

Magnetic properties

From the shift $A$ one gets either ($\chi_e \sim \chi_0$). $V$

or $\omega$ or both (in the case where $\Phi(h) = P(h_1, h_2)$). With a known anisotropy or intensity of magnetization one can determine particle size from this measurement (Ref. 3). On the other hand, if the particle size is determined independently, the magnetic properties can be deduced.

Anisotropy and optical anisotropy

The method of determining saturation values of the parameters ($Q_L \sim Q_R$) and $\delta$ from the experimental data is
already given before, since \((Q_L - Q_R)_{\infty}\) and \((\delta)_{\infty}\) are related jointly to the particle shape and its possibly anisotropic refractive index, it is useful to investigate how \((Q_L - Q_R)_{\infty}\) and \((\delta)_{\infty}\) are influenced by:

1. Departure from sphericity as indicated by the difference \((L_e - L_o)\),
2. The absorption of the particle, and
3. The anisotropy of its refractive index.

With respect to the last point, unfortunately, only the data pertaining to the birefringence are available for different crystalline material (i.e. the real parts \(n_e\) and \(n_o\), but data pertaining to crystalline dichroism (i.e. the imaginary parts \(n'_e\) and \(n'_o\)) are not available. We assume therefore, that crystalline absorption is isotropic. Also, since in the present work only absorbing materials are investigated, the term \(\frac{2}{3}i\kappa^3|\alpha|^2\), which is contribution of scattering to the extinction, is neglected. Of the four cases discussed, two groups must clearly be separated.

(I) In case I and III, the particles orient parallel to the direction of field. Therefore,

\[
(Q_L - Q_R)_{\infty} = 3 \text{Im} \left[ \frac{\alpha_e - \alpha_O}{\alpha'_O + 2\alpha_O} \right]
\]
This gives $\Im \frac{\alpha}{\alpha_o} = \frac{3 + 2X}{3 - X}$ where $X = (\xi L - \xi R)_\infty$

$$[\delta]_\infty = 2\pi \mu \cdot H \cdot \Re (\alpha - \alpha_o) \cdot \left[ \frac{2\pi L}{\lambda} \right]$$

This gives $\frac{4\pi}{V} \left[ \Re (\alpha - \alpha_o) \right] = (\delta)_\infty \cdot \frac{\lambda \phi}{\pi \mu \cdot M \cdot L} \quad (N = \frac{M}{V \phi})$

(II) In case II and IV, when the particles orient perpendicular to the direction of field, one gets:

$$(\xi L - \xi R)_\infty = \frac{3}{2} \Im \left[ \frac{\alpha - \alpha_o}{\alpha + 2\alpha_o} \right]$$

This gives $\Im \frac{\alpha}{\alpha_o} = \frac{3 - 4X}{3 + 2X}$ where $X = (\xi L - \xi R)_\infty$

$(\delta)_\infty$ and $\frac{4\pi}{V} \left[ \Re (\alpha - \alpha_o) \right]$ are now given by the expressions

$$(\delta)_\infty = 2\pi \mu \cdot L \cdot \Re \left[ \frac{\alpha - \alpha_o}{2} \right] \cdot \left[ \frac{2\pi L}{\lambda} \right]$$

$$\frac{4\pi}{V} \left[ \Re (\alpha - \alpha_o) \right] = (\delta)_\infty \cdot \left[ \frac{-2\lambda \phi}{\pi \mu \cdot M \cdot L} \right] \quad (N = \frac{M}{V \phi})$$

In the following pages are discussed some more general cases which are based on the equation

$$\alpha_j = \frac{V}{4\pi} \left[ \frac{1}{1 + \frac{1}{L_j + \frac{1}{m_j^2 - 1}}} \right] ; \tilde{m}_j = m_j - im_j$$

(A) Absorbing, isotropic, non-spherical particles

Here, $m_e = m_o = m ; L_e \neq L_o ; (L_e - L_o) = \Delta L$
This gives \[ \frac{\text{Im } \alpha}{\text{Im } \alpha_0} = \left[ 1 - \frac{L(m^2 - 1)}{L_0(m^2 + 1)} \right] \]

\[ = \left[ 1 + 3AL \left( \frac{m^2 - 1}{m^2 + 2} \right) \right]^2 \text{ if } L_0 \approx \frac{1}{3} \]

In birefringence the particles are assumed to be non-absorbing, isotropic and non-spherical in shape, so \( \text{Re}(\alpha_0 - \alpha) \) will be:

\[ \text{Re}(\alpha_0 - \alpha) = \frac{V}{4\pi} \left[ \frac{3(m^2 - 1)}{(m^2 + 2)^2} \right] (L_0 - L_0) \]

i.e., \[ \text{Re}(\alpha_0 - \alpha) = 3 \left[ \frac{(m^2 - 1)}{(m^2 + 2)^2} \right] \Delta L \]

where \( \Delta L = (L_0 - L_0) \)

To get an idea of the order of magnitude; if \( (L_0 - L_0) = 0.05 \), then for \( m = 2.35 \) (corresponding to \( \alpha-\text{Fe}_2\text{O}_3 \) - hematite crystal) and \( 0.05 \) (\( m^1 \langle 0.3 \):

\[ \frac{\text{Im } \alpha}{\text{Im } \alpha_0} = \left[ 1 - 3(0.05) \left( \frac{(2.35)^2 - 1}{(2.35)^2 + 2} \right) \right]^2 \]

\[ = 0.91 \]

(1) i.e., \( IM_{\alpha} = 0.91 = \frac{3 - 2X}{3 - X} \) where \( X = (Q_L - Q_R) \alpha \)

\[ \therefore X = -0.093 \text{ i.e. } (Q_L - Q_R) \alpha = 0.093 \text{ for parallel orientation} \]
Thus, \((Q_L - Q_R) = 0.093\) for parallel orientation

\((Q_L - Q_R) = 0.0465\) for perpendicular orientation

Since such an order of magnitude for \((Q_L - Q_R)\) is fairly large, it is concluded that appreciable anisometry should give rise to strong magneto-optical effects. Such strong effects were observed, particularly, in iron oxide (hydrated) and copper ferrite sols.

(B) Absorbing, anisotropic spheres

Effects are now entirely due to crystalline anisotropy. Ideally one should now use two complex indices,

\[
\bar{m}_o = m_o - \imath n_o
\]

\[
\bar{m}_e = m_e - \imath n_e
\]

Available data, however, relate only to \(m_o\) and \(m_e\) and no data are available for \(n_e\) and \(n_o\). We, therefore, assume \(m_e \approx m_o\). It is realized, however, that in actual cases
these two indices may be markedly different. Simplifying the expression for \( \bar{\alpha}_e \) and \( \bar{\alpha}_c \), one gets in this case:

\[
\frac{\mathrm{Im} \bar{\alpha}_e}{\mathrm{Im} \bar{\alpha}_c} = \left[ \frac{\frac{L_o (m_e^2 - 1) + 1}{L_o (m_e^2 - 1) + 1}}{\frac{m_e}{m_o}} \right]^{2} \cdot \left( \frac{m_e}{m_o} \right)
\]

\[
= \left[ \frac{(m_e^2 - 1) + 3}{(m_e^2 - 1) + 3} \right]^{2} \cdot \left( \frac{m_e}{m_o} \right)
\]

if \( L_e = L_c = \frac{1}{3} \)

In the case of birefringence, the expression will be

\[
\frac{4 \Pi}{V} \cdot \left[ \Re \left( \bar{\alpha}_e - \bar{\alpha}_c \right) \right] = \frac{18 \pi L_o \delta}{(m^2 + 2)^2}
\]

Here it is assumed:

\[
m_e \neq m_o ; \ m_e = m ; \ m_o = (m_e - \delta) ; \ L_e = L_c = \frac{1}{3}
\]

As a specific case for iron oxide sol (-vely charged) which is strongly birefringent: \( m_e = 2.21 \); \( m_o = 2.421 \) (v.r.t. water)

\[
\frac{\mathrm{Im} \bar{\alpha}_e}{\mathrm{Im} \bar{\alpha}_c} = \left[ \frac{\frac{3.3612 + 3.0}{3.9341 + 3.0}}{\frac{m_e}{m_o}} \right]^{2} \cdot \left( \frac{2.21}{2.421} \right)
\]

\[
= 1.0423
\]

\[
\therefore \frac{3 + \frac{2X}{3}}{3 - X} = 1.0423 \quad \therefore \ X = 0.042 \text{ for parallel orientation}
\]
Thus, \( Q_L - Q_R \approx 0.0423 \) for parallel orientation

\( (Q_L - Q_R)_\infty \approx 0.0248 \) for perpendicular orientation

So, it can be concluded that (in the absence of crystalline dichroism) the optical anisotropy results in comparatively weaker magneto-optical effects.

(iii) Anisotropic, anisometric absorbing particles:

It is assumed that the geometrical symmetry axis is coincident with the optical symmetry axis. It is also assumed that the proper absorption in the particles is isotropic but its refractive index is anisotropic.

If absorption term \( m^2 \) is not very large (so that \( m^2 \) can be neglected) at the same time absorption is the dominant extinction process, we get

\[
\frac{\text{Re}(\alpha_e - \alpha_o)}{\frac{\text{Im} \alpha_e}{\text{Im} \alpha_o}} = \frac{\frac{\text{Im}(\alpha_e^2 - 1)}{\text{Im}(\alpha_o^2 - 1) + 1}}{\left[ \frac{\alpha_e^2 - 1}{\text{Im}(\alpha_e^2 - 1) + 1} - \frac{\alpha_o^2 - 1}{\text{Im}(\alpha_o^2 - 1) + 1} \right]}
\]

When \( m^2 \) exceeds about 0.3, complete expressions must
be used for calculations, with $\alpha_j$ given by equation on page 79.

In the case of $\alpha$-$Fe_2O_3$, the two principal refractive indices are known fairly reliably viz. $n_e = 2.16$; $n_o = 2.21$ w.r.t. water and therefore, these anisotropic refractive indices are used for calculation.

Figures 9 and 10 are constructed for the ratio \[ \frac{\text{Im } \alpha_e}{\text{Im } \alpha_o} \] and the difference $\alpha_\circ (\alpha_e - \alpha_o)$. Figure No. 10 contains the graphs constructed for $\alpha$-$Fe_2O_3$ particles. From the observed values of $(\epsilon_\circ - \epsilon_\text{H})$, $(\delta_\circ)$, $\frac{\text{Im } \alpha_e}{\text{Im } \alpha_o}$ and $\frac{\text{Im } \alpha_o}{\text{Im } \alpha_e}$, \[ \Re(\alpha_e - \alpha_o) \] were first calculated and $L_e$, $L_o$ are, then, read from the above graphs and then the shape (i.e. ratio $a/b$) is deduced using the figure 11.

In the case of other colloids, isotropic refractive index is used (figures 9, 10). Since ferrites crystallize in a spinel structure which has a cubic symmetry, they are expected to be optically isotropic apart from the slight induced anisotropy due to magneto-striction.
Figure No. 11  Depolarization Coefficient
vs. Shape factor

L_e vs. \( \alpha_d \)
# REFERENCES

1. Naik, Y.C., Desai, J.N., Shah, M.S.  
   (1968), 6, 282.

2. Mehta, J.V.  
   Ph.D. Thesis (1968) Gujarat University  
   C3, pp. 124-133.

3. Naik, Y.C., Desai, J.N.  
   (1965), 2, 27.