Theory of the Optical and Magnetic Properties of Ferromagnetic Suspensions

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The theory of the optical transparency of ferromagnetic suspensions, as modified by magnetic fields, is developed along lines suggested by C. W. Heaps. It is proposed to determine the average "shape" of the particles by measuring the transmission of a suspension in various directions while the particles are magnetically aligned parallel to one another. From this information, the complete magneto-optic behavior of the suspension can be deduced; comparison between experimental and theoretical curves gives a value of the (average) magnetic moment of the particles. In addition, theory for two new magneto-optic experiments is developed, one which will give directly the intensity of magnetization of the particles, the other which will give directly the volume of the particles. In the first experiment changes in transparency are used to indicate when the particles have been rotated magnetically through a definite angle; the second experiment is based on the changes in transparency accompanying the return to random particle orientation following the removal of an applied magnetic field. It is shown that suspensions should have a transmission of $(1/e)$ to give a maximal magneto-optic effect.

A CELL containing a suspension of particles of magnetite acts in a limited way as a magnetically controlled light shutter. This effect, discovered nearly a century ago by W. R. Grove,[1] recently has been rediscovered and studied by C. W. Heaps.[2] The latter made measurements of cell transmission with respect to magnetic field intensity, and attempted to account for the variation in transmission on the following basis. (1) The magnetite particles possess permanent magnetic moments. (2) Magnetically linked groups of particles are responsible for the effect and they cast shadows characteristic of a cylinder. (3) The particle groups behave as a classical paramagnetic gas. From these assumptions Heaps deduced that the cell transmission should approach a limiting value proportional to $H^{-\frac{1}{2}}$; his experimental findings, however, failed to agree with this deduction. In a short note[3] the writer showed that by assuming spheroidal rather than cylindrical particle groups the transmission should vary as H^{-1} for intense fields, and that Heaps' data are in fair accord with this prediction, the computed value of μ being 1.4×10^{-12} e.m.u. This value would seem to indicate that the particle groups, estimated by Heaps to average 5 microns in diameter, have a very small intensity of magnetization. The conclusion is of interest, for it appears likely that much smaller particles of magnetite exist as single ferromagnetic domains.[4]

Since the light shutter action of ferromagnetic suspensions affords a simple method of studying the remanent magnetization of small ferromagnetic particles, it appears worth while to reconsider the theory of the phenomenon, and to carry out experiments with a variety of ferromagnetic suspensions and colloids. The present paper, therefore, will be devoted to modifying and to extending Heaps' theory, particularly in the direction of devising new experiments which will give additional information concerning the magnetization of ferromagnetic particles. A second paper is planned which will be devoted to new experimental results.

VARIATION IN TRANSPARENCY WITH MAGNETIC FIELD INTENSITY

A small particle in a beam of light removes light by scattering and by absorption, thereby possessing a certain effective cross section Q which is defined as the ratio of the total energy per second removed by the particle from the light beam to the intensity of the beam. For a particle of a given size, shape and orientation the value of Q may depend on the wave-length of light, on the optical properties of the material constituting the particle, and on the refractive

[1] See discussion by L. W. McKeehan, Phys. Rev. **57**, 1177 (1940).
[2] C. W. Heaps, Phys. Rev. **57**, 528 (1940).
[3] W. C. Elmore, Phys. Rev. **57**, 842 (1940).
[4] W. C. Elmore, Phys. Rev. **54**, 1092 (1938).

index of the medium in which the particle is immersed. In general, Q will differ from the geometrical cross section of the particle even though the particle be opaque. In view of the dependence of Q on wave-length, the following theory will hold strictly only for the transmission of monochromatic light through a ferromagnetic suspension or colloid. However, the theory may be applied safely to measurements made with white light, provided that the light is not colored appreciably by the suspension.

Let n be the number of particles per unit volume in the suspension, and let Q be their average effective cross section. The fraction of light removed by a layer of the suspension of thickness dx is $dl/l=-nQdx$, so that the transmission t of a cell of length L is

$$t=e^{-nLQ}, \qquad (1)$$

which is, of course, Beer's law.[5] Since the particles are permanently magnetized, and since they are not in general perfect spheres (a "particle" may be a magnetically linked group of the ultimate particles of the suspension), the value of Q, and hence that of t, will depend on the direction and magnitude of an applied magnetic field. Let $Q_{||}$ be the average value of Q when all particle moments are lined up parallel to the optic axis of the cell, and let us define the average relative cross section $q\equiv Q/Q_{||}$, thus referring all cross sections to $Q_{||}$. Experimental values of q may be computed from measured transmissions by the relation

$$q=\log t/\log t_{||}, \qquad (2)$$

which follows immediately from Eq. (1). Since it will be found convenient to make all comparisons between theory and experiment by means of curves of relative cross section, all derivations regarding transparency of suspensions will be left as formula for q, Eq. (2) being implied.

Let us denote by $q_\infty(\psi)$ the relation connecting the average relative cross section for completely aligned particles with the angle ψ between the aligning field and the cell axis. Then the value of q for any field H making an angle α with the cell axis can be determined by the extension of Langevin's theory of a paramagnetic gas suggested by Heaps. For this calculation it is convenient to use spherical coordinates, with the polar axis in the direction of the magnetic field, and let the angle between the particle moments and the field be specified by the polar angle θ and the azimuth ϕ. In these coordinates the light axis can be specified by $\theta=\alpha$, $\phi=0$, so that the value of ψ in $q_\infty(\psi)$ is related to θ and ϕ by $\cos\psi=\sin\alpha\,\sin\theta\,\cos\phi+\cos\alpha\,\cos\theta$. Hence the dependence of q on $a\equiv\mu H/kT$ and on α is given by

$$q(a,\alpha)=\frac{\int_0^{2\pi}\int_0^{\pi} q_\infty(\psi)e^{a\cos\theta}\sin\theta d\theta d\phi}{\int_0^{2\pi}\int_0^{\pi} e^{a\cos\theta}\sin\theta d\theta d\phi}. \qquad (3)$$

Before proceeding further, it is necessary to have an expression for $q_\infty(\psi)$. Instead of assuming that the form of the average particle cross section is similar to that of a cylinder or of a spheroid, it is more satisfactory to determine its form by measuring cell transmission as a function of ψ. By symmetry one expects that the experimental data can be expressed by the series

$$q_\infty(\psi)=1+q_1\sin^2\psi+q_2\sin^4\psi+\cdots \qquad (4)$$

where q_1, q_2, $\cdots$ are constants. Now it will be shown in a subsequent paper that in many cases only two constants, q_1 and q_2, are required to fit Eq. (4) to the measured curve of $q_\infty(\psi)$. Hence all calculations based on (4) will be carried only through the term containing q_2. On substituting (4) in (3) and performing the integration, one obtains an expression governing the response of the light cell to a magnetic field of arbitrary magnitude and direction. Only the results for $\alpha=0$ and for $\alpha=\pi/2$ will be given here, since they possess the greatest experimental interest. By writing $L(a)\equiv\coth a-1/a$, the two results become, respectively,

$$q(a,0)=1+q_1(2/a)L(a)+q_2\{8/a^2-(24/a^3)L(a)\}, \qquad (5)$$

and

$$q(a,\pi/2)=1+q_1\{1-(1/a)L(a)\}+q_2\{1-(2/a)L(a)+(3/a^2)[1-(3/a)L(a)]\}. \qquad (6)$$

In the foregoing theory, all quantities except μ can be determined experimentally. To test the

[5] In his theory Heaps assumed that $t=1-nLQ$. This is not a good approximation to Beer's law for transmissions differing appreciably from unity.

theory plots of Eqs. (5) and (6) can be compared with the experimental curves of relative cross sections against magnetic field intensity. Provided that the distribution in particle moments is not too broad, the two sets of curves should coincide when the value of μ is correctly chosen.

To obtain the intensity of magnetization of the particles from the value of μ it is necessary to know the particle volume. Now the microscope will give only a rough estimate of this volume if the particle diameter is less than one micron. The sedimentation method based on Stokes law cannot be used, for, on standing, the particles in the suspension tend to form larger and larger magnetically linked groups. For the same reason the method based on counting particles in a suspension of known concentration is unsatisfactory. It is possible, however, to perform other experiments with the light cell which will give, independently, the intensity of particle magnetization, and the volume of the particles. These two results can then be compared with the value of the particle magnetic moment obtained in the first experiment.

Variation in Transparency with Time Following a Change in Field Direction

Let r be the mean particle radius and η the coefficient of viscosity of the suspending liquid. Then, according to Stokes law for rotation, the torque required to turn a particle at constant angular velocity $d\psi/dt$ is $8\pi r^3\eta d\psi/dt$. Consider the case where the suspended particles are magnetically aligned in some particular direction. If, now, the direction of the field is suddenly shifted, the torque acting on any one particle is $\mu H\sin\psi$ where ψ is the angle between μ and H. Hence we must have $8\pi r^3\eta d\psi/dt=\mu H\sin\psi$ since the inertial term is negligible. Let us integrate this equation for a change in field direction of $\frac{1}{2}\pi$, thus obtaining

$$\tau=\frac{8\pi r^3\eta}{\mu H}\int_{\frac{1}{2}\pi}^{\theta}\frac{d\psi}{\sin\psi}=\frac{8\pi r^3\eta}{\mu H}\ln|\tan(\theta/2)|, \quad (7)$$

which gives the time τ required for the particles to turn through an angle $\frac{1}{2}\pi-\theta$. If we write $\mu=(4\pi/3)r^3I$, where I is the intensity of magnetization of the particles, we obtain from Eq. (7)

$$I=(6\eta/\tau H)\ln|\tan(\theta/2)|, \quad (8)$$

a result *independent of the size of the particles*. By suspending the particles in an aqueous glycerol solution, a wide range of values of η are available. Values of τ for various field strengths can be obtained by measuring the time required for the particles to rotate through a particular angle as indicated by the change in transparency of the suspension. Hence we have a simple method for determining directly the average intensity of magnetization of the particles.

Variation in Transparency During Relaxation

Einstein has shown[6] that rotational Brownian motion obeys the diffusion equation with the coefficient of rotational diffusion given by

$$D=kT/4\pi r^3\eta. \quad (9)$$

Let us apply this concept to determine the changes in transparency following the removal of a magnetic field applied parallel to the cell axis. When the field is present, the distribution of particle moments is given by $\nu=\text{Const. } e^{a\cos\theta}$ where ν is the number of particle moments per unit solid angle making an angle θ with the magnetic field. To obtain an expression governing the relaxation of this distribution to a random one, we must solve the diffusion equation

$$\frac{\partial\nu}{\partial t}=\frac{D}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\nu}{\partial\theta}\right), \quad (10)$$

subject to the boundary conditions that at $t=0$, $\nu=\text{Const. } e^{a\cos\theta}$ and at $t=\infty$, $\nu=\text{Const.}$ Now the elementary solutions of (10) have the form

$$e^{-n(n+1)Dt}P_n(\cos\theta),$$

where $n=0, 1, 2, \cdots$ and $P_n(\cos\theta)$ is a Legendre polynomial. By means of the integral

$$\int_{-1}^{+1}e^{ax}P_n(x)dx=(2\pi/a)^{\frac{1}{2}}I_{n+\frac{1}{2}}(a),$$

where $I_{n+\frac{1}{2}}(a)$ is a modified Bessel function, it is easy to obtain the expansion

$$e^{a\cos\theta}=(\pi/2a)^{\frac{1}{2}}\sum_{0}^{\infty}(2n+1)I_{n+\frac{1}{2}}(a)P_n(\cos\theta),$$

[6] See, for instance, R. H. Fowler, *Statistical Mechanics* (Cambridge, 1936) p. 774.

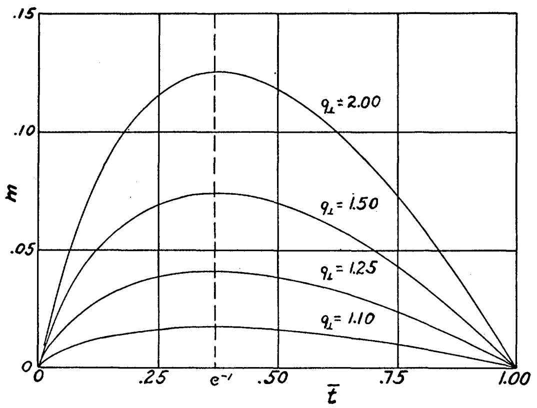

FIG. 1. Illustrating the dependence of modulation on transmission for several shapes of particles.

so that the solution of (10) which satisfies the required boundary conditions is

$$\nu(\theta,t)=\text{Const.}(\pi/2a)^{\frac{1}{2}}\sum_0^\infty(2n+1)I_{n+\frac{1}{2}}(a)\times P_n(\cos\theta)e^{-n(n+1)Dt}. \quad (11)$$

Finally, the time variation in the average relative cross section during relaxation will be given by a calculation similar to Eq. (3),

$$q(t)=\frac{\int_0^\pi q_\infty(\theta)\nu(\theta,t)\sin\theta d\theta}{\int_0^\pi \nu(\theta,t)\sin\theta d\theta}, \quad (12)$$

where $q_\infty(\theta)$ is given by Eq. (4) with $\psi=\theta$.

To evaluate Eq. (12) it is convenient to rewrite Eq. (4) in the form

$$q_\infty(\theta)=c_0+c_2P_2(\cos\theta)+c_4P_4(\cos\theta)+\cdots, \quad (13)$$

where the new constants c_i are related to the old constants q_i as follows:

$$\left.\begin{array}{l} c_0=1+(2/3)q_1+(8/15)q_2+\cdots \\ c_2=-(2/3)q_1-(16/21)q_2+\cdots \\ c_4=(8/35)q_2+\cdots \\ \cdots\cdots\cdots\cdots \end{array}\right\}. \quad (14)$$

Hence Eq. (12) becomes, on integrating,

$$q(t)=[1/I_{\frac{1}{2}}(a)]\sum c_nI_{n+\frac{1}{2}}(a)e^{-n(n+1)Dt}, \quad (15)$$

where the summation is to be taken for $n=0, 2, 4, \cdots$, the number of terms depending on the number of constants in Eq. (13) [or in Eq. (4)] required to represent the experimental of curve of $q_\infty(\theta)$. For purposes of computation Eq. (15) may be written in terms of hyperbolic functions by means of the well-known formulae for modified Bessel functions of half-integral order. A case interesting from the experimental standpoint arises when a is very large, i.e., when initially all particles are aligned parallel to the cell axis. Since for large a, $I_{n+\frac{1}{2}}(a)\rightarrow(1/2\pi a)^{\frac{1}{2}}e^a$, Eq. (15) becomes

$$q(t)=c_0+c_2e^{-6Dt}+c_4e^{-20Dt}+\cdots. \quad (16)$$

By comparing the observed changes in transparency during relaxation with those predicted from Eq. (15) or (16) it is possible to obtain a value of the rotational diffusion constant D. By means of Eq. (9) the volume (average) of the particles may then be computed.

BEST VALUE OF TRANSMISSION FOR EXPERIMENTAL STUDIES

It is helpful to know what transmission suspensions should have to be best suited for experimental study. Let us define the average transmission of a cell by $\bar{t}=\frac{1}{2}(t_{||}+t_\perp)$ and the modulation (maximum) of the cell by $m=\frac{1}{2}(t_{||}-t_\perp)$, where the subscripts refer to the direction of the magnetic field with respect to the cell axis. On using (1) and (2), and maximizing m with respect to nL, it is found that

$$\left.\begin{array}{l} \bar{t}=\frac{1}{2}(q_\perp+1)q_\perp^{-q_\perp/(q_\perp-1)}\doteq(1/2e)(q_\perp+1), \\ m=\frac{1}{2}(q_\perp-1)q_\perp^{-q_\perp/(q_\perp-1)}\doteq(1/2e)(q_\perp-1), \end{array}\right\} \quad (17)$$

where $q_\perp\equiv\log t_\perp/\log t_{||}$, and where the approximate expressions hold for values of $q_\perp$ not differing much from unity, a situation which is (unfortunately!) always true. Hence it is concluded that the greatest changes in transmission are produced by a magnetic field when the cell transmits about $(1/e)$ of the light which it would transmit if it contained pure liquid. In Fig. 1 is illustrated the dependence of modulation on transmission for several values of $q_\perp$.