Chapter V  
Magnetic Field Dependent Backscattering of Light in  
Water Based PAA Covered Fe$_3$O$_4$ Nanofluid

5.1 Introduction

Wave propagation through ordered and weakly disordered scattering media have been explored in the past [341-344]. Experimentally, the phenomenon of weak localization of light has been widely studied in coherent backscattering from colloidal suspension [345], cold atom gases [346], disordered liquid crystals [347], disordered micro cavities [348], etc. Also, the backscattering and vanishing of energy transport velocity have been studied by Pinheiro et al [225, 226]. The interaction of light with disordered particles provides new ways to probe nonlinear optical effects, optical bistability, etc. which are important for the future technologies such as bistable switching devices, neural optical computers, etc..

In this chapter, we probe the magnetically induced changes in backscattered light intensity and speckle profiles in ferrofluid during structural transitions. First, the external field induced variations of backscattered speckle pattern and speckle contrast are analyzed. Then the possible reasons for the field induced changes in the backscattered light intensity and its angular dependence are investigated. Subsequently, the tuning behavior of backscattered light intensity is also discussed.

5.2 Experimental Details

The details of the ferrofluid samples used in this study are explained in Chapter II (section 2.2). The backscattered light intensity is measured as a function of $B$ using the experimental set up shown in Figure 2.4. The direction of $B$ was perpendicular to the incident light direction in this case. The experimental details for acquiring the backscattered light intensity and speckle patterns from the samples as a function of $B$ are explained in Chapter II (section 2.3).
5.3 Results and Discussions

5.3.1 Field Induced Backscattered Speckle Dynamics in Ferrofluid

Fig. 5.1. (a - d) Images of backscattered light from ferrofluid at different external magnetic fields ($B = 0, 100, 165, 283$ G) and the corresponding (e - h) phase contrast microscopic images of ferrofluid at the same external fields.

Figure 5.1 (a – d) show the images of backscattered light from ferrofluid in presence of different magnetic field values of 0, 100, 165 and 283 G. It is observed that the light intensity diminishes with increasing $B$. Figure 5.1 (e - h) shows the phase contrast microscopic images of ferrofluid observed under similar $B$. In the presence of $B$, the magnetic nanoparticles in water form aligned structures when the magnetic coupling constant, $\Lambda_{coup}$ (Eq. 3.3 in Chapter III) is much greater than one. The speckles observed in the backscattered light images are shown in Figures 5.1 (a – d). As $\lambda$ ($\approx 632.8$ nm) and beam width ($\approx 1\text{mm}$) of the incident light are larger than the size of the nanoparticles (diameter, $d \approx 15\text{nm}$), constructive and destructive
interferences of the scattered light wavelets from all possible scattering trajectories produce intensity fluctuations, which are called speckles, as shown in Figures 5.1 (a-d). The speckle pattern resulting from a medium is its fingerprint and is being exploited in speckle imaging or diffuse wave spectroscopy [244, 308, 309]. Piederriere et al. [349] have shown that the backscattered speckle size (produced by strongly-scattering liquid media such as monodisperse polystyrene microspheres in solutions, mixtures of different sized microspheres, milk, blood and pig skin) depends on the scattering and anisotropy coefficients. The backscattered light images [Fig. 5.1 (a-d)] from ferrofluid show that the speckle intensities diminish with increasing $B$ as the nanoparticles form long chains [Fig. 5.1 (e – h)].

Fig. 5.2. (a) Variation of speckle contrast ($C$) of backscattered speckles with external magnetic fields ($B$). Images (b, d, f, h): backscattered light at different external magnetic fields from ferrofluid and images (c, e, g, i) are the corresponding 3D surface plots.
Figure 5.2(a) shows the variation of $C$ of the backscattered light with $B$ which is calculated by using the intensity values at different fields shown in the images (c, e, g, i) of Figure 5.2 and by using Equation 4.5 (Chapter IV). The linear increase in the backscattered $C$ with $B$ indicates a transformation of ‘dynamic’ to nearly static speckle pattern due to the formation of chainlike structures.

5.3.2 Field Induced Variations of Backscattered Light Intensity and Possible Reasons for Extinction of Backscattered Light

![Graph showing variation of backscattered light intensity over time for different magnetic field ramp rates.]

Fig. 5.3. Variation of backscattered light intensity as a function of time ($t$) at different magnetic field ramp rates. Backscattered angle, $\theta_b = 179.8^0$, $\phi \sim 0.00816$. 
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Figure 5.3 shows the backscattered light intensity from ferrofluid as a function of time for different field ramp rates, at a fixed backscattering angle ($\theta_b = 179.8^\circ$) and $\phi = 0.00816$. The backscattered light intensity decreases in presence of $B$ and the rate of decrease is found to be faster for higher field ramp rates. The possible reasons behind the lowering of backscattered light intensity with $B$ are discussed below.

In absence of $B$, the ferrofluid behaves as a disordered soft matter with no birefringence or circular dichroism [61, 218]. The application of magnetic field induces magneto-optical anisotropy such as birefringence, transmittivity, Faraday rotation and Cotton-Mouton effect [350, 351]. Theoretical studies show that coherent backscattering is altered by Faraday rotation and natural optical activity in a medium of inhomogeneities smaller than the wavelength [352, 353]. Experimental observation shows that the maximum Faraday shift is $\sim 2^0$ at $B = 150$ Gauss [183]. Such shift can affect the backscattering but it does not cause such a dramatic change of backscattered light intensity. Also, optical absorption studies in ferrofluid show the absence of absorption peaks in the visible region and hence in the weak $B$ ($0 < B < 600$ G) region, absorption does not have a role in the extinction of backscattered light [183].

With increasing $B$, the size of the scatterers increases due to dipolar attractions that can result in an increase in the length of $\ell^*$ [271]. At some critical fields, the scatterer sizes are such that resonances occur in the anisotropy factor $\langle \cos \theta \rangle$ and in the extinction efficiency factor $(Q_{ext})$ [183]. The field dependent resonant behaviors cause the building up of standing waves inside the scatterer and results in an extra delay in light transmission through ferrofluid. Such resonances might cause the extinction of backscattered light intensity in presence of a magnetic field.

According to Mie scattering theory, the backscattered efficiency $(Q_b)$ is given by[286],
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\[ Q_b = \frac{1}{(ka)^2} \left| \sum_{n=1}^{\infty} (2n+1)(-1)^n (a_n - b_n) \right|^2 \]  

(5.1)

where the scattering parameters \((a_n \text{ and } b_n)\) are given by,

\[ a_n = \frac{m_{MF}^2 j_n(m_{MF}x)[x j_n(x)]' - \mu j_n(x)[m_{MF}x j_n(m_{MF}x)]'}{m_{MF}^2 j_n(m_{MF}x)[x j_n^{(1)}(x)]' - \mu j_n^{(1)}(x)[m_{MF}x j_n(m_{MF}x)]'} \]  

(5.2)

\[ b_n = -\frac{\mu j_n(x)[x j_n(x)]' - j_n(x)[m_{MF}x j_n(m_{MF}x)]'}{\mu j_n^{(1)}(x)[x j_n^{(1)}(x)]' - \mu j_n^{(1)}(x)[m_{MF}x j_n(m_{MF}x)]'} \]  

(5.3)

where, \(m_{MF}\) is the external magnetic field dependent refractive index of the ferrofluid [224] and the functions \(j_n(z)\) and \(h_n^{(1)}(z) = j_n(z) + iy_n(z)\) are the spherical Bessel functions of order \(n(n=1,2,\ldots)\) and of the given arguments, \(z = x\) or \(m_{MF}x\), respectively, and primes signify derivatives with respect to the arguments.

The size parameter \((x = ka)\) increases with \(B\) due to aggregation of nanoparticles. Using Equations (5.1) to (5.3), the backscattering efficiency \((Q_b)\) as a function of \(x = ka\) is calculated and is shown in Figure (5.4). The resonant behavior of the backscattering efficiency with size parameter is evident from Figure (5.4). The inset of Figure (5.4) shows the zoomed view at lower \(ka\) values. Similar Mie resonances in forward-backward anisotropy factor with size parameter have been observed earlier [183]. The external field dependent resonant states in backscattered efficiency and forward-backward anisotropy factor that introduces a delay in light propagation inside the medium due to the formation of standing waves would have resulted in the observed extinction of backscattered light. As the evolution into chainlike structures from magnetic nanoparticles becomes more rapid with increasing magnetic field ramp rate, the rate of decrease in backscattered intensity is more [235].
Fig. 5.4. Backscattered efficiency ($Q_b$) as a function of size parameter ($ka$). Inset figure shows the enlarged view of variation of $Q_b$ within small values of $ka$. 
5.3.3 Angular Variation of Backscattered Light in Presence of External Magnetic Field

Fig. 5.5. Angular variation of backscattered light intensity from ferrofluid in presence of external magnetic field at a ramp rate of 1 G/s.

The field induced aggregation process in ferrofluid leads to a reduction in the backscattered light intensity within small backscattered angular range [i.e. within $\theta_s - \Delta \theta_b < \theta_s < (\theta_s + \Delta \theta_b)$] where $\Delta \theta_b$ is the small angular change from $\theta_s = 180^\circ$]. In Figure 5.5, it is observed that a small change in the backscattered angle leads to large changes in the backscattered intensity.

For an infinite cylinder, by using diffraction theory approximation, the phase function $p(\theta, \varphi)$ which is the function of the total light scattered into a unit solid angle in a given direction $\theta, \varphi)$ is[286],

\[ p(\theta, \varphi) = \frac{1}{4\pi} \int_{0}^{2\pi} \int_{0}^{\pi} \frac{\sin \theta'}{\sin \theta} \cdot p(\theta', \varphi') \, d\theta' \, d\varphi' \]
$$p(\theta) = \frac{\pi}{4x} \left[ 1 + \cos \theta \frac{x \sin(x \sin \theta)}{\pi x \sin \theta} \right]^2$$

(5.4)

For backscattered light from a cylindrical surface, the backscattered phase function $p(\theta_b)$ decreases with change in the backscattered angle.

Fig. 5.6. Plot of backscattered phase function $p(\theta_b)$ and backscattered light intensity with $\Delta \theta_b$ from $\theta_b = 180^0$. $p(\theta_b)$ varies as $(\Delta \theta_b)^{-2.84}$ with size parameter, $ka = 1000$. The variation of normalized backscattered light intensity from ferrofluid with $\Delta \theta_b$ from $\theta_b = 180^0$ is measured at $B = 472G$. 

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Figure 5.6 shows the variation of backscattered phase function $p(\theta_b)$ with $\Delta \theta_b$ where $p(\theta_b)$ decays with $\Delta \theta_b$ as $\sim \Delta \theta_b^{-2.84}$ for fixed size parameter, $x=1000$. The variation of backscattered light with change in backscattered angle ($\Delta \theta_b$) for an external field, $B = 472$ G (obtained from Figure 5.5) also shows decay behavior with $\Delta \theta_b$, though considerable deviation from the theoretical curve [$p(\theta_b)$ vs $\Delta \theta_b$] is observed. Therefore, the observed decrease in the backscattered phase function $p(\theta_b)$ with an increase in $\Delta \theta_b$ is in reasonable agreement with the theory. This explains the angular dependence of backscattered light intensity in presence of $B$.

5.3.4 Tunability of Backscattered Light

![Ramp rate - 8 G/s](image)

Fig. 5.7 Tunable backscattering of light from ferrofluid in presence of external magnetic fields with $\theta_b = 179.8^0$ and field ramp rate 8 G/s.
Figure 5.7 shows the field induced tunable behavior of backscattered light from ferrofluid. Here, the measurements are done in presence of $B$ on ferrofluid of $\phi = 0.00816$ at fixed $\theta_b = 179.8^0$ and ramp rate (8 G/s). The backscattered light intensity recovers to the original level with a small hysteresis. This result shows that the aggregation process is reversible. The area between the intensity curves during the ‘increase’ and ‘decrease’ is defined as the hysteresis area. Physically, the variation of hysteresis area between the ‘increase’ and ‘decrease’ of external field is due to the difference in the aggregate size during these processes. During ‘increase’, nanoparticle aggregates are formed, which de-aggregate upon removal of the external field because of the dominance of thermal energy due to Brownian motion. The initial time ($t_c$) for two particles to aggregate is $t_c = \frac{a}{5} \frac{6\pi a \eta}{F_{\text{max}}} ((\frac{r_1}{2a})^5 - 1)$ where the magnetic force between the particles at contact is given by $F_{\text{max}} = \frac{\mu_0}{4\pi} \frac{3m^2}{8a^4}$, $r_1$ is the initial separation distance between the particles and $\eta$ is the viscosity of the carrier liquid[235, 282]. The time required for aggregation of the particles and linear aggregates in a carrier liquid for a given external field depends on two competing forces experienced by them: the magnetic force due to field induced magnetic moment and the viscous force. The magnetic force depends on the particle size, number of particles in the linear aggregates and external field strength, whereas the viscous force depends on the particle or aggregate size and viscosity of the carrier liquid. Therefore, for a given sample concentration, the aggregation time changes with the change of external field strength. The dispersed magnetic particles in a carrier liquid can relax either by particle rotation in the liquid by Brownian relaxation with a rotational diffusion time given by $\tau_B = 3V_h \frac{\eta}{k_B T}$, where $V_h$ is the hydrodynamic particle volume and $\eta$ is the viscosity of the carrier liquid. The rotation of the magnetic vector within the particle by Neel relaxation
mechanism occur with a characteristic time ($\tau_N$) is
\[
1 \geq \frac{1}{f_0} \exp\left(\frac{KV_m}{k_BT}\right) \text{ for } \frac{KV_m}{k_BT} << 1,
\]
where $f_0$ is the attempt frequency of magnetization, $K$ is the anisotropy constant of the material, and $V_m$ is the magnetic volume of the particle [59, 82, 354]. The typical Brownian and Neel relaxation times for the dispersed particles in the present ferrofluid are about $10^{-7}$ and $10^{-9}$ s, respectively. The value of $\tau_N$ increases sharply with the size of the particle due to the exponential dependence on $V_m$. This reversible behavior of backscattered light intensity with external magnetic field provides a new approach to fabricate tunable photonic devices using ferrofluid.

5.4 Conclusions

The evolution of backscattered speckle pattern during field induced structural arrangements of magnetic nanoparticle dispersion is investigated experimentally for the first time. The backscattered speckle contrast increases towards its saturation value with external field, which signifies a nearly static speckle pattern by losing the scatterers movement due to aggregation. The backscattered light intensity decreases with external magnetic field due to the delay in the light propagation inside ferrofluid owing to the formation of standing waves inside the scatterers. It is observed that a small change in backscattered angle gives rise to a large variation in the backscattered light intensity in the presence of an external magnetic field. The reversibility in the backscattered light intensity offers possibilities of exploiting such ferrofluids for photonic device applications.
6.1 Introduction

Absorption is the study of interaction of waves with matter, which is probably the most widespread and precise analytical technique used to study isolated atoms, molecules, small clusters in gas, condensed phases, bio molecules, and the structures and dynamics of quantum systems from atomic domain to natural proteins[355-357]. Infrared absorption spectroscopy is a powerful technique for in-situ analysis of chemical, bio-medical and nano-fluidic systems [358-360]. Aggregation processes of dielectric and metal nanoparticles were also studied using infrared absorption spectroscopy [361, 362]. Saito et al. [185] measured the optical attenuation constants of magnetic nanofluid at infrared region during field induced aggregation of magnetic nanoparticles in dispersion.

Recently, optical properties of nanofluids have been a topic of intense research due to their fascinating properties and interesting applications [63, 199, 222, 320, 363]. Among nanofluids, magnetic nanocolloid possess the unique property of tunability of particle interaction by external magnetic field, which makes it an attractive candidate for fundamental research and has enormous applications in optical domain [150, 152, 160, 229, 271, 364, 365]. Extinction coefficient of magnetic fluids has been studied in detail using spectral transmittance approach and molecular dynamics simulation where it has been shown that the extinction coefficient increases with increasing particle volume fraction and particle diameter (for a fixed volume fraction) [366, 367]. Heterodyne interferometry technique has also been used for studying the low magnetic field induced tiny variations in the complex refractive index for anisotropic and opaque magnetic fluid thin film specimens [368].

In this chapter, the behavior of near infrared (NIR) photon absorption by a magnetically polarizable oil-in-water emulsion or nanoemulsion in presence of an external magnetic field is
studied. The near infrared absorption as a function of sample volume fraction and external magnetic field is probed. Also, using the near infrared absorption profile in the Rayleigh regime, the imaginary part of the refractive index \( (k) \) of magnetic nanoemulsion, that depends on the sample volume fraction and external magnetic field, is evaluated for the first time.

6.2 Experimental Details

The nanoemulsion samples used in this study is a disordered magnetic medium as explained in Chapter II (section 2.2). The detailed procedure of acquiring the absorption spectra through the samples as a function of \( B \) is explained in Chapter II (section 2.4). Here the direction of incident light is parallel to the direction of \( B \).

6.3 Results and Discussions

6.3.1 Near Infrared (NIR) Light Absorption by Nanoemulsion

Fig. 6.1. Phase contrast microscopic images of nanoemulsion at different external magnetic fields \( (B = 0, 70, 100, 160, 220G) \).

Figure 6.1 shows the phase contrast microscopic images of the nanoemulsion observed at different \( B \) (0 to 220 G). The direction of \( B \) is shown by the arrow. It can be seen that at zero field the nanoemulsion droplets are randomly oriented and as \( B \) increases, the droplets orient themselves along the direction of \( B \) leading to a chain like structure. In magnetic nanoemulsion, oil droplets are electro-statically stabilized with sodium dodecyl sulphate (SDS). When the droplet double layer is very thin \( (\kappa z l_1 < S) \), the electrostatic force profile follows the equation
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\[ F_n (r_i) = 4\pi \varepsilon_i \varepsilon_0^2 a_i^2 \left[ \frac{\kappa}{r_i} + \frac{1}{r_i^2} \right] \exp[-\kappa(r_i - 2a_i)] \]  

(6.1)

where \( a_i (= \frac{d}{2}) \) is the droplet radius, \( r_i \) is the droplet separation distance, \( \varepsilon_1 \) is the dielectric permittivity of the suspending medium, \( \zeta_0 \) is the electrical surface potential and \( \kappa \) is the inverse Debye length that depends on the electrolyte concentration \( (C_e) \) and can be represented as \( \kappa^{-1} = \left( \frac{1}{4\pi} \right) [2L_B^2C_e]^{0.5} \), where ‘\( L_B \)’ is the Bjerrum length [62, 64].

In presence of \( B \), when the ratio of the dipolar interaction strength to thermal energy, is much greater than one \( (\Lambda_{coup} >> 1) \) (as discussed in Chapter III, Section 3.2.1), the nanoemulsion droplets in dispersion undergo an disorder-order transition, i.e. Brownian to a linear chain-like structure- with head-on aggregation along the \( B \) direction which is shown in Figure 6.1.

Figure 6.2(a) shows the absorption of near infrared (NIR) photons by nanoemulsion as a function of photon energy \( (E) \) for \( \phi = 0.0014, 0.0019, 0.0022, 0.0067 \) in the absence of \( B \). Here, the absorption linearly increases with \( E \) and \( \phi \), which indicate that absorption increases with the number density \( (\rho_n) \) of nanoemulsion droplets in the dispersion \( (\phi = \rho_n \varrho) \), where \( \varrho \) is the droplet volume [369]).
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Fig. 6.2. (a) Near infrared (NIR) photon absorption \(A\) with photon energy \(E\) (in eV) at zero external field by nanoemulsion with different volume fraction, \(\phi = 0.0067, 0.0022, 0.0019,\)
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0.0014. Solid lines correspond to linear regression analysis of the experimental data. (b)
Absorption coefficient ($\alpha$) as a function of photon energy at different $\phi = 0.0067$, 0.0022, 0.0019, 0.0014 of nanoemulsion. Solid lines correspond to linear regression analysis of the calculated data from (a).

Here the emulsion droplet size ($d \sim 220$ nm) is much smaller than the $\lambda$ of the NIR photons ($\lambda = 800–1100$ nm) and according to Rayleigh scattering theory ($d < \lambda$), the absorption cross-section ($C_{abs}$) is given by the relation: $C_{abs} = \alpha \nu$, where, $\alpha = \frac{4\pi k_1}{\lambda}$ is the absorption coefficient, $k_1$ is the imaginary part of the refractive index ($m = n_1 + ik_1$) of the nanoemulsion [286]. The real part of the refractive index ($n_1$) of the nanoemulsion indicates the speed and the imaginary part ($k_1$) signifies absorption losses during the propagation of an electromagnetic wave through the medium [286]. The absorption cross-section is related to the $E$ as

$$C_{abs} = \frac{4\pi \nu k_1}{hc} \times E$$

(6.2)

where $h$ is the Plank’s constant. It is clear from Equation 6.2 that $C_{abs}$ increases linearly with increasing $E$ in the Rayleigh regime. It is evident from Figure 6.2a that the higher energy infrared photon causes more absorption for all $\phi (=0.0067, 0.0022, 0.0019, 0.0014)$ of the nanoemulsion samples. It must be noted that, Figure 6.2a actually shows that absorption ($A$) increases with $\phi$ and the relation between $A$ and $\alpha$ is [370]

$$\alpha = \frac{2303A \rho_n}{\phi L}$$

(6.3)

where $\rho_n$ is the density of the nanoemulsion droplet and $L$ is the optical path length (~1mm). From Equations 6.2 - 6.3 it is evident that $A$ is directly proportional to $\alpha$ and $C_{abs}$. 92
Figure 6.2b shows $\alpha$ as a function of $E$ for the nanoemulsion specimens of four different $\phi$. $\alpha$ values are obtained from the absorption values (Fig. 6.2a) using Equation 6.3. It can be seen from Figure 6.2b that $\alpha$ increases with $\phi$ due to the increase in number density of the nanoemulsion droplets. It is further observed from Figure 6.2b that $\alpha$ increases linearly with $E$ which is expected from Equations 6.2 – 6.3. The solid lines in Figure 6.2b indicate the linear regression analyses of the experimental data and the slopes of these linear fits provide the average values of the imaginary part of the refractive index ($k_1$) of nanoemulsion samples.

### 6.3.2 Magnetic Field Dependent NIR Light Absorption by Nanoemulsion

Figures 6.3 a & b show absorption ($A$) as a function of incident photon energy ($E$) for a nanoemulsion of $\phi = 0.0019$ in the presence of $B$. As $B$ increases from (0 to 60G), $A$ is found to increase over the entire energy range. But from 70 to 250G, the $A$ of NIR photons decreased. Figure 6.3c shows the linear increase of absorption ($A$) with $E$ (eV) at different $B$ ($= 0, 45, 50, 60$ G). This figure is similar to Figure 6.2a, where $A$ linearly increases with $E$. But beyond 65 G, the variation of $A$ with $E$ is not linear (Fig. 5.3b). Hence, from Figure 6.2a and Figure 6.3c it can be inferred that the field induced increase in $A$ up to 65 G follows Rayleigh scattering theory (scatterer size $< \lambda$).
Fig. 6.3. Absorption ($A$) as a function of incident photon energy ($E$, in eV) at different external magnetic fields ($B$) by nanoemulsion ($\phi \sim 0.0019$). (a) $B$ varies from 0 to 65 G, (b) $B$ varies from 70 to 250 G, and (c) $A$ vs. $E$ plot for $B = 0, 45, 50, 60$ G and best linear fit.

According to Rayleigh scattering theory, higher the energy of the incident photon more is the absorption (Eq. 6.2). This is evident from Figure 6.3c under the presence of $B$ (up to 65 G).
The field induced increase in the absorption of NIR photons was also observed with increasing $\phi$.

Figure 6.4a shows the absorption of NIR photons as a function of magnetic field for different $E$ at $\phi = 0.0019$. From zero to $\sim 30$ G, the increase in absorption is found to be negligible, but beyond 30 G the absorption increases rapidly with $B$. It has been earlier shown that for very low $B$ ($B < 30$ G), the nanoemulsion specimen remains opaque and field induced chain like structures do not form [229]. Hence, below 30 G absorption remains almost constant, whereas, for $B > 30$ G, absorption increases due to formation of external field induced chain like structures. Beyond $B \sim 80$ G, absorption decreases with $B$. It is observed that absorption is significantly higher for photons with higher energy up to 65 G. Figure 6.4b shows the continuous evolution of absorption of NIR photons of energies 1.55, 1.46 and 1.38 eV with $B$ where it shows that up to $\sim 80$ G, absorption of NIR photons increases with $B$. From Figure 6.4b it can be seen that (i) peak value of absorption increases with increasing $E$ and (ii) the absorption peak shifts to lower $B$ with increasing $E$. With increasing $E$, the $\lambda$ decreases and hence, absorption increases in the Rayleigh regime (Eq. 6.2), which leads to higher absorption peak values with increasing $E$. 
Fig. 6.4. (a) Absorption of different energy ($E = 1.55$, 1.50, 1.46, 1.42, and 1.38 eV) NIR photons as a function of external magnetic field ($B$) for nanoemulsion ($\phi = 0.0019$). (b) The continuous change of external field induced absorption of NIR photons with energies $E = 1.55$, 1.46, and 1.38 eV.

The position of the absorption peak for particular $E$ signifies transition from Rayleigh to Mie regime for the corresponding $\lambda$. For decreasing $E$, the field induced aggregate size comparable to the corresponding $\lambda$ increases and the required $B$ for the Rayleigh to Mie transition also increases. Hence, absorption peak shifts to lower $B$ with increasing $E$. 
6.3.3 Field Induced Variations of Imaginary Part of the Refractive Index ($k_1$) of Nanoemulsion

Fig. 6.5. Imaginary part of refractive index ($k_1$) of nanoemulsion as a function of external magnetic fields for different volume fraction, $\phi = 0.0014, 0.0019, 0.0022, 0.0067$. Inset: $k_1$ as a function of $\phi$ at zero field.

The $k_1$ values at different $B$ are obtained from the slopes of the best fit curves of $\alpha$ vs. $E$ plots for different $B$ and $\phi$ (From Fig. 6.3c for $\phi = 0.0019$ at different $B$). In a magnetic nano-colloid
the refractive index depends on the concentration of magnetic nanoparticles in dispersion and $B$ [224, 371]. Figure 6.5 shows the variation of $k_1$ values with $B$ at different $\phi$. It is observed that $k_1$ values increase with $\phi$ at fixed $B$ ( = 0, 45, 50, 60 G). The inset of Figure 6.5 shows the variation of $k_1$ as a function of $\phi$ at zero external field. It is also observed that for a particular volume fraction, $k_1$ increases with $B$. These observations can be explained by the fact that absorption increases due to two different reasons, viz. increase in number density (i.e. $\phi$) of the nanoemulsion and external field induced chain like structure formation. Figure 6.6 shows the plot of the calculated $k_1$ values with theoretical $k_1$ values at four different $\phi$ at zero external field. The slope of the linear regression analysis is nearly unity which shows that the experimentally calculated values are in good agreement with the theoretical values. This shows that NIR absorption profiles can be used for the accurate estimation of $k_1$ of the nanoemulsion.

It must be noted that the above mentioned methodology is valid only in the Rayleigh regime (i.e. for $B$ up to 65 G). Beyond Rayleigh regime, the scattering follows Mie theory due to increased sizes of field induced aggregates.
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Fig. 6.6. Variation of the calculated values of $k_1$ with theoretical values obtained using Eq. 6.2. Slope of the linear fit is $0.90 \pm 0.07$. Volume fractions, $\phi \sim 0.0014, 0.0019, 0.0022$ and 0.0067.

Fig. 6.7. $k_1$ as a function of $\phi$ at (a) zero $B$, (b) 45G, (c) 50G, (d) 60G. $k_1$ follows a power law ($k_1 \sim \phi^p$) dependence with $\phi$ for different $B$, where the exponent ($p$) values are 0.70, 0.58, 0.53, 0.48 at 0, 45, 50, 60G, respectively.

Figure 6.7 shows the variation of $k_1$ with $\phi$ for different $B$. It can be seen from the Figure that $k_1$ increases with $\phi$ for different $B$. It was further observed that the increase in $k_1$ with $\phi$
follows a similar trend in all the cases and the data are fitted using a power law: $k_1 \sim \phi^p$, where the exponents ($p$) are 0.70, 0.58, 0.53, 0.48 at 0, 45, 50, 60 G, respectively. Figure 6.8 shows the variation of $p$ with $B$ where $p$ decreases linearly with increasing $B$ with a maximum at zero field. In presence of $B$, the nanoemulsion droplets undergoes a disorder to order transition and chain like structures along the direction of $B$ start growing, which increases the absorption of NIR photons. The decreasing values of $p$ with increasing $B$ indicates the formation of chain like ordered structures and field induced increase in absorption of NIR photons.
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Fig. 6.8. Exponent \( (p) \) values as a function of external magnetic fields \( (B) \). Solid line corresponds to linear regression analysis.

6.3.4 Explanation of Magnetic Field Dependent Variations of NIR Light Absorption

Based on Mie Theory

The field induced aggregation of nanoemulsion droplets due to dipolar attraction increases the scatterer sizes (Fig. 6.1 b–e) and when the scatterer sizes are comparable to or higher than the \( \lambda \) of NIR photons, the interactions of NIR photons with such scatterers are beyond the Rayleigh regime and fall in the Mie regime.

According to Mie scattering theory, the absorption efficiency \( (Q_{\text{abs}}) \) is given by [285, 286]

\[
Q_{\text{abs}} = \frac{4 e^{\varepsilon''}}{x^2} \int_0^x <|E_1|^2 > x'^2 dx'
\]  

(6.4)

where, \( x = ka_f \) is the size parameter, \( e'' \) is the imaginary part of the relative dielectric constant of the scatterers, \( E_1 \) is the electric field component of the incident near infrared photons and

\[
<|E_1|^2 > = \frac{1}{4} \sum_{n=1}^{\infty} (m_n |c_n|^2 + n_n |d_n|^2)
\]  

(6.5)

where the Mie scattering parameters are given by

\[
c_n = \frac{\mu_1 j_n (x)[x h_n^1 (x)]' - \mu_1 h_n^1 (x)[x j_n (x)]'}{\mu_1 j_n (m_1 x)[x h_n^1 (x)]' - h_n^1 (x)[m_1 x j_n (m_1 x)]'}
\]  

(6.6)

\[
d_n = \frac{\mu_1 m_1 j_n (x)[x h_n^1 (x)]' - \mu_1 m_1 h_n^1 (x)[x j_n (x)]'}{m_1^2 j_n (m_1 x)[x h_n^1 (x)]' - h_n^1 (x)[m_1 x j_n (m_1 x)]'}
\]  

(6.7)

and

\[
m_n = 2(2n+1)|j_n(z)|^2, \ n_n = 2n(2n+1) \left\{ (n+1) \left( \frac{j_n(z)}{z} \right)^2 + \left( \frac{z j_n(z)}{z} \right)^2 \right\}
\]
where, \( m_1 \) is external magnetic field dependent refractive index of the nanoemulsion [224, 371], \( \mu_1 \) is the ratio of the magnetic permeability of the nanoemulsion droplets to that of the dispersion medium. The function \( j_n(z) \) and \( h_n^1(z) = j_n(z) + iy_n(z) \) are the spherical Bessel functions of order \( n \) \((n = 1, 2, \ldots)\) and primes signifies derivatives.

The size parameter \((x = ka)\) increases with \( B \) due to the aggregation of nanoemulsion droplet in the dispersion. Using Equations 6.4 – 6.7, the \( Q_{abs} \) as a function of size parameter for three different \( E \) (=1.55, 1.46, 1.38 eV) is computed and shown in Figure 6.9.
Fig. 6.9. Absorption efficiency \( Q_{\text{abs}} \) as a function of size parameter \( (ka_1) \) for different photon energy \( (E = 1.55, 1.46, \text{and} \ 1.38 \text{eV}) \). Inset: Magnified view of the continuous variation of \( Q_{\text{abs}} \) with \( ka_1 \) for \( E = 1.55, 1.46, \text{and} \ 1.38 \text{eV} \).

The inset of Figure 6.9 shows the increasing nature of the \( Q_{\text{abs}} \) at lower \( ka_1 \). At lower values of \( ka_1 \), according to the Rayleigh scattering theory, \( Q_{\text{abs}} \) and \( C_{\text{abs}} \), which is directly related to absorption, increase with \( B \), which is in good agreement with the experimental observations (Figs. 6.3 – 6.4). It can be observed from Figure 6.4 that the absorption of NIR photons of different energy increases up to 65G, where the nanoemulsion droplets in the dispersion forms short chain like structures (Figs. 6.1b-c). Beyond \( B = 65 \text{ G} \), the short chains form longer chain-like structures (Figs. 6.1d-e) along the \( B \) direction and absorption starts decreasing (Fig. 6.4). The \( Q_{\text{abs}} \) for NIR also starts decreasing above \( ka_1 \sim 3.79 \) (inset of Fig. 6.9). With the increase in \( B \), the chain length increases due to head to tail aggregation of emulsion droplets (Figs. 6.1c-e). Simultaneously, the space between the chains also increases which decreases the effective scattering cross section and \( Q_{\text{abs}} \). The decreasing trend in \( Q_{\text{abs}} \) with size parameter (Fig. 6.9) explains the decay of absorption of NIR photons in nanoemulsion beyond \( B = 65 \text{ G} \) (Fig. 6.3 and 6.4).

6.4 Conclusions

The effect of external magnetic field on the NIR photon absorption in nanoemulsion is investigated. The absorption depends on the sample volume fraction and in presence of an external magnetic field, the NIR photon absorption by nanoemulsion increases up to a critical external magnetic field and beyond that the absorption decreases which is attributed to the change in Mie absorption efficiency. Up to a critical external magnetic field, the dimensions of field induced aggregates are smaller than the wavelengths of the interacting NIR photons.
(Rayleigh regime), where the imaginary part of the refractive index of nanoemulsion increases with sample volume fraction. The calculated $k_1$ follows a power law increment with sample volume fraction ($k_1 \sim \phi^p$, where $p$ is the exponent) where $p$ linearly decreases with external magnetic field, which clearly indicates that the field induced structural ordering of nanoemulsion droplets significantly contribute towards the absorption of NIR photons. Beyond the Rayleigh regime, the field induced increment in the aggregate length and inter chain distance between aggregates resulted in a reduction in the NIR absorption.