Path length tunable light-matter interaction in magnetic nanofluid based field-induced photonic crystal-glass structure

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Abstract
The ability to control the light–matter interaction and the simultaneous tuning of both the structural order and disorder in materials, although important in photons, remain major challenges. In this paper, we demonstrate that path length dictates light–matter interaction for the same crystal structure, formed by the ordering of magnetic nanoparticle self-assembled columns inside magnetic nanofluid under applied field. When the path length is shorter \( L = 80 \ \mu \text{m} \), the condition for maintaining temporal coherence for the constructive interference is therefore satisfied, resulting in the formation of a concentric diffraction ring pattern; while for a longer path length \( L = 1 \ \text{mm} \), only a corona ring of scattered light is observed. Analysis of diffraction ring pattern suggests the formation of 3D hexagonal crystal structure, where the longitudinal and lateral inter-column spacings are 5.281 \( \mu \text{m} \) and 7.344 \( \mu \text{m} \), respectively. Observation of speckles and diffuse scattering background within the diffraction ring pattern confirms the presence of certain degree of crystal disorder, which can be tuned by controlling the applied field strength, nanoparticle size and particle volume fraction. Our results provide a new approach to develop next generation of tunable photonic devices, e.g. tunable random laser, based on simultaneous harnessing of the properties of disordered photonic glass and 3D photonic crystal.

1. Introduction
Colloidal particles can self-assemble into various ordered periodic structures under favorable conditions (e.g. screened colomic repulsive interactions, volume fractions, pH, temperature etc), which makes colloid a model soft condensed matter system to study the crystallization thermodynamics of atomic and molecular systems [1–6]. In order to study colloidal crystals, visible light diffraction has been routinely used as a diagnostic tool, since the length scale of the colloidal crystal is of the order of visible wavelength [7–10]. It also enables a potential route for the fabrication of three dimensional (3D) photonic crystals that can be used to control and manipulate light in three dimensions [11–15]. The disorder due to structural artifacts present in any photonic crystal gives rise to multiple scattering, which limits their technological applications [16]. To overcome this issue, the recent focus is on harnessing the multiple scattering, in order to introduce new functionalities, which opens up a completely new perspective on disorder in photonic crystals, e.g. random lasers employing photonic glasses containing a completely disordered arrangement of monodisperse colloids [16–19]. Hence, reversible tuning of disordered colloidal particles (photonic glass) into a 3D photonic crystal or vice versa with an external stimulus will have huge technological implication.

Magnetic nanofluid, popularly known as ferrofluid, is a promising colloidal system that offers interesting optical and photonic properties, due to the ability to reversibly change the internal structural ordering under an applied magnetic field [20–29]. The magnetic nanofluid is a stable dispersion of magnetic nanoparticles in a carrier liquid, where nanoparticles undergo random Brownian motion in the absence of any external field. On
applying external magnetic field \((H_0)\), the magnetic nanoparticles in the dispersion acquire dipole moment \((m)\) given by

\[
m = \frac{\pi}{6} d^3 \chi H_0
\]

Here, \(d\) is the particle diameter, \(\chi\) is the effective susceptibility of an individual nanoparticle. The dipolar interaction energy \(U_{ij}\) between two magnetic nanoparticles is given by

\[
U_{ij} (r_{ij}, \theta_{ij}) = \frac{m^2 \mu_0}{4\pi} \left( \frac{1 - 3 \cos^2 \theta_{ij}}{r_{ij}^3} \right)
\]

where \(\mu_0\) is the magnetic permeability of free space, \(r_{ij}\) is the magnitude of the vector describing the distance between the centers of \(i\)th and \(j\)th nanoparticles, and \(\theta_{ij}\) is the angle between the vector \(r_{ij}\) and the external magnetic field vector. The effective interaction energy between two magnetic nanoparticles is determined by the competition between the dipolar interaction energy \(U_{ij} (r_{ij}, \theta_{ij})\) and the thermal energy \((k_B T)\), hence, can be described by

\[
\Lambda = \frac{U_{ij} (r_{ij}, \theta_{ij})}{k_B T}
\]

Here, \(k_B\) is the Boltzmann constant and \(T\) is the temperature. When \(U_{ij} (r_{ij}, \theta_{ij})\) becomes greater than \(k_B T\), i.e. when \(\Lambda > 1\), linear aggregates, i.e. chains are formed due to the self-assembly of nanoparticles along the applied field direction. With further increase in field strength \((H_0)\), the chains of nanoparticles undergo lateral aggregation, known as zipper aggregation, due to the nanoparticle chain fluctuation induced short range attraction to minimize the total dipolar potential energy of the system [30]. Therefore, the application of external field leads to complex structural changes inside the magnetic nanofluid that gives rise to interesting optical properties, as discussed below.

As the magnetic field increases, the scatterer size increases from single nanoparticle diameter to the dimensions of columns of nanoparticles, which lead to an increase in the scattering efficiency, thereby resulting in a decrease in the transmitted light intensity [31]. However, for a given volume fraction \((\phi)\) and applied field strength \((H_0)\), the transmitted light intensity decreases on increasing the path length \((L)\) [32]. When the scatterer shape changes from spherical (single nanoparticles) to the cylindrical shape (columns), the scattered pattern changes from a single laser spot to a corona like ring, with the transmitted laser spot on the ring circumference, for a longer path length \((L = 1 \text{ mm})\) [31, 33]. However, for very short path length \((L \leq 10 \mu\text{m})\), the interaction of the white light with the structural periodicity due to two dimensional (2D) hexagonal crystal ordering results in chromatic diffraction rings [23, 34, 35].

The path length dependent field induced column spacing is studied in oil-in-water ferrofluid emulsions of relatively larger oil droplet size \((>100 \text{ nm})\) [36]. The field induced crystal ordering is observed to be 2D hexagonal in magnetic nanofluid with small particle size \((\sim 11.8 \text{ nm})\) for very short path lengths \((L \leq 10 \mu\text{m})\) [34]. On increasing the path length to \(L \approx 0.5 \text{ mm}\) for magnetic nanofluid with larger core–shell structure nanoparticles \((>100 \text{ nm})\), the field induced crystal ordering changes to 3D hexagonal [22]. However, the field induced crystal structure for the intermediate path length range, i.e. \(10 \mu\text{m} < L < 0.5 \text{ mm}\) and the spacing among the columns of nanoparticles for longer path lengths \((L > 10 \mu\text{m})\) in magnetic nanofluids are still unknown; owing to experimental constrains and lack of stable suspensions with long term stability, which is a prerequisite to observe reversibly tunable optical properties. As a result, an understanding of the role of path length on the magnetic field induced crystal ordering and the resulting optical properties such as diffraction, light transmission, scattering, speckle pattern, Fano resonance etc are still missing [23, 31, 37–45].

Moreover, the structural studies carried out so far have been limited to magnetic nanofluids of relatively larger magnetic particle size (diameter \(d > 100 \text{ nm}\)) and higher concentration (volume fraction, \(\phi > 0.1\)), i.e. shorter inter-particle distance \((r_{ij})\), which leads to a stronger dipolar interaction \((U_{ij})\) (equation (2)) among the magnetic nanoparticles [22]. This results in the sedimentation of particles even in the absence of external magnetic field, therefore, limiting the possibility to tune colloidal crystalline order to create photonic crystals [46]. Therefore, use of lower volume fraction and smaller particle size compared to the probing light wavelength \((d \ll \lambda)\) will ensure that the observed light–matter interaction phenomena, e.g. diffraction do not originate from the inter-particle spacing, rather from the spacing of ordered linear aggregates formed by nanoparticle aggregation under applied field; besides providing the possibility to tune the structure from completely random to ordered.

In this study, we have addressed the following questions regarding tunable light–matter interaction in magnetic nanofluid under external field in the context of photonics: (a) Is the light–matter interaction tunable by controlling path length? (b) What is the field induced crystal structure in the intermediate path length range, i.e.\(10 \mu\text{m} < L < 0.5 \text{ mm}\)? (c) What is the implication of disorder present in the ordered crystal structure on the light–matter interaction?
2. Material and method

2.1. Magnetic nanofluid sample
We synthesized a highly monodisperse (polydispersity index, PDI ~ 0.092) and stable magnetic nanofluid which consists of very small superparamagnetic magnetite (Fe₃O₄) particles (diameter, d ~ 6.7 nm) with a surfactant layer (oleic acid, layer thickness ~1.5 nm) for the present study [31, 38]. The volume fraction used for the nanoparticles dispersed in the carrier liquid kerosene was very low (ϕ = 0.017 13).

2.2. Experimental section
A stabilized He-Ne laser (Spectra-physics,117A) of wavelength λ ~ 632.8 nm with an output power ~4.5 mW (coherence length >100 m, spectral linewidth ~3 MHz) is used as a light source. An external magnetic field (H₀ ~ 300 G) is applied along the incident light direction by keeping the cell containing the magnetic nanofluid sample inside a solenoid [31]. The light scattered patterns are acquired on a translucent screen, kept at a distance of 11.8 cm from the sample cell by using a digital single lens reflex (DSLR) camera, for two path lengths (L = 1 mm and 80 μm) of the sample cell. Details of the experimental technique and schematic of the experimental set up are described elsewhere [31, 38].

3. Results and discussion

3.1. Observed light scattered (corona ring) and diffraction pattern (concentric rings)
For the longer path length (L = 1 mm), a single corona ring with the transmitted laser spot on the ring circumference is observed in the scattered pattern, as shown in figure 1(a). However, for the shorter path length (L = 80 μm), concentric diffraction rings with the transmitted laser spot at the center is observed in the scattered pattern, as shown in figure 1(b). Although, the complete ring circumference is visible for the innermost diffraction ring, the light intensity and the visible radial angle range of the ring circumference gradually decreases for the outer rings. Speckle patterns are observed along the broad circumferential widths of the diffraction rings and in the intermediate space among the rings. The innermost and the other three concentric outer rings are designated as 1st, 2nd, 3rd and 4th ring for the analysis purpose.

3.2. Origin of single corona like scattered ring
The single corona ring formed for the longer path length, L = 1 mm (figure 1(a)) originate from the light scattering by the surface of the cylinder shaped columns of aggregated nanoparticles, formed along the applied field direction [31, 33]. When light interacts with a cylindrical surface, the resulting outgoing scattered light takes the shape of a scattered light cone, whose intersection on a screen placed perpendicular to the incident light forms a conic section, as shown in figure 2(a). The shape dependence of the conic section, on the incident angle (ζ) with respect to cylinder axis, is explained by deriving the expression of scattered electromagnetic field from cylindrical surface [47]; which leads to the conclusion that the surfaces of constant phase, or wave fronts, of the scattered waves are the points that satisfy the condition

\[ f(x, y, z) = r \sin \zeta - z \cos \zeta = C \]  

Therefore, the wave fronts are cones of half-angle ζ with their apexes at

\[ z = -C/\cos \zeta \]  

The propagation of the scattered waves can be visualized as a cone that is sliding down the cylinder. The direction of propagation at any point on the cone, or wave normal \( \hat{e}_s \) is

\[ \hat{e}_s = \nabla f = \sin \zeta \hat{e}_r - \cos \zeta \hat{e}_\zeta \]  

The Poynting vector is therefore, in the direction \( \hat{e}_s \). From equations (5) and (6), it is clear that on placing a screen at some distance from the cylinder and perpendicular to the incident light, the resulting scattered pattern forms a conic section. When the light is incident along the applied field direction, i.e. at near zero degree to the field induced cylindrical column axis (ζ ≈ 0°), the scattered pattern becomes a circle, as shown in figures (1(a) and 2(a)). For angles of incidence less than 45°, ellipse appears on the screen, as observed for (ζ = 30°) in figure 2(c). When the incident light is normal to the cylinder axis (ζ = 90°), the scattered pattern becomes a straight line (figure 2(d)).

Figures 2(e)–(g) shows the microstructural evolution of the field induced structures at three different magnetic field strengths in a ferrofluid emulsion with a droplet size ~200 nm. Ferrofluid emulsion of this size is chosen in order to observe the microstructure using a simple phase contrast optical microscope. In the case of magnetic nanofluid, visualization of such structure formation is not possible with an optical microscope, owing
to their small size. The increase in the length of the chains formed by the aggregation of nanoparticles is evident from the microscopic images.

3.3. Reason for observing concentric diffraction ring pattern only for shorter path length ($L = 80 \mu m$)—Role of maintaining temporal coherence

Constructive interference among the scattered lights from the parallel lattice planes of an ordered crystal structure results in the observation of interference fringes, the diffraction pattern of concentric rings, as shown in figure 1(b). The interference fringes will be formed only if the time delay among the interfering scattered light waves is such that

$$\Delta t \Delta \nu \leq 1,$$

which is the condition for maintaining temporal coherence among the interfering light waves [48]. In other words, the formation of interference fringes is the manifestation of temporal coherence among the scattered light waves. Here, $\Delta \nu$ (~3 MHz) is the spectral linewidth of the incident light; $\Delta t$ is the time delay introduced among the scattered light waves from different parallel lattice planes. The span of the crystal structure, i.e. the path length of magnetic nanofluid along the incident light and applied field direction, has strong implication on the time delay ($\Delta t$) among the scattered lights, therefore, on the formation or absence of interference fringes (concentric diffraction rings) on the observation plane. For the shorter path length ($L = 80 \mu m$), $\Delta t$ is shorter, therefore, the condition (equation (7)) for constructive interference is easily satisfied, resulting in the observation of concentric diffraction rings, as shown in figure 1(b). However, on increasing the path length ($L = 1 \text{ mm}$), due

Figure 1. Light scattered patterns of magnetic nanofluid ($\phi = 0.017 13$, $d = 6.7 \text{ nm}$) under applied magnetic field ($H_0 \sim 300 \text{ G}$) for two path lengths ($L$). (a) Single corona ring for $L = 1 \text{ mm}$ and (b) diffraction ring pattern for $L = 80 \mu m$. The (c) and (d) are the 3D surface intensity distribution plots of (a) and (b), respectively. The direction of the applied magnetic field is along the incident light propagating through the path of the sample cell.
to the increased time delay ($\Delta t$) among the scattered lights, the interference condition is no longer satisfied, therefore, only a scattered light pattern (single corona ring) is observed, as shown in figure 1(a).

3.4. Analysis of magnetic field induced crystal structure

The observation of the diffraction rings (figure 1(b)), for path length ($L = 80 \mu m$), confirms the formation of a crystalline structure by the field induced columns. The continuous circumferences of the 1st and 2nd rings indicate that the formed structure is polycrystalline, irrespective of the type of crystal lattice. The broader width of the ring, unlike the sharp diffraction rings for atomic crystals, and the speckle pattern within the diffraction pattern indicate that the crystal ordering is not perfect, rather has a certain degree of structural disorder, due to the reasons explained in details in section 3.5 [49, 50].

3.4.1. Field induced crystal structure analysis on considering 2D hexagonal crystal

In order to find out the exact crystal structure in the present case ($L = 80 \mu m$), as a first approximation, the field induced crystal structure is assumed to be a 2D hexagonal, as observed earlier for a very short path length ($L \leq 10 \mu m$) [23, 34]. A 2D crystal acts as a two dimensional diffraction grating and the resulting diffraction rings pattern follows [10, 49]
$d_{hk} \sin \theta = n \lambda \quad \text{(8)}$

where $\lambda$ is the incident light wavelength, $n$ is the diffraction order (an integer), $d_{hk}$ is the spacing between the parallel lattice planes, more appropriately parallel lattice lines for 2D crystals designated by the Miller indices $(hk)$. Here, the reflection angle $(\theta)$ is the angle between the incident light and the lattice planes. Therefore, each diffraction ring, observed at a particular diffraction angle $(\theta_{d})$, results from the constructive interference of the light scattered from a particular family of parallel lattice planes $(hk)$ of the crystal structure.

The diffraction angle $(\theta_{d})$ corresponding to each diffraction ring (figure 1(b)) is determined by measuring the sample to screen distance (11.8 cm) and the ring radius. For this purpose, the light intensity of each diffraction ring is integrated over the entire radial angle $[0^\circ–360^\circ]$ by considering the transmitted laser spot as the origin, and plotted as a function of the diffraction angle $(\theta_{d})$ for each peak. This is due to the presence of a background formed by scattered light that is observed within the diffraction pattern (figure 1(b), also shown in the inset of figure 3(b)).

3.4.2. Origin of the background light observed within the diffraction pattern formed by the scattered light

The two types of scattering discussed below contribute to the background light. Firstly, diffuse scattering due to the presence of certain degree of crystal disorder of first type, originating from the thermal fluctuation of the field induced columns at the lattice vertices, as discussed in details later in section 3.5 [30, 51, 52]. Crystal disorder of first type manifests as the decrease in diffraction peak intensity; the lost scattering light intensity is redistributed into diffuse scattering within the diffraction pattern [51, 53]. Secondly, Mie scattering by the magnetic field induced columns (the crystal lattices), as the column dimensions are of the order of the incident light wavelength $(\lambda \sim 632.8 \text{ nm})$ (figure 1(b)) [31]. Basically, the observed diffraction pattern (figure 3(a)) is an overlap of the
diffraction and the background scattered light. In fact, the scattered light background also contributes to the finite light intensity in the dark band regions among the bright diffraction rings (figure 3(a)). The intensity of the background scattered light decreases with increase in scattering angle [54], which is the diffraction angle (θd) in figure 3(a); this is why the intensity peaks (figure 3(a)) become less asymmetric in shape with increase in diffraction angle (θd). Therefore, the scattered light background is subtracted from the observed diffraction pattern (figure 1(b)) in order to correct the maximum intensity positions (diffraction angles (θd,θf)) of the diffraction intensity peaks. The diffraction intensity peak shapes become symmetric after the background corrections, as shown in figure 3(b). The inset of figure 3(b) shows the diffraction pattern after subtracting the scattered light background.

The center positions for the first three diffraction intensity peaks are determined by Gaussian fit. The obtained peak center positions also coincided very well with the center of the circumferential widths of the concentric diffraction rings. The diffraction angle (θd) corresponding to the fourth ring is determined by positioning a circle along the center of ring circumferential width (inset of figure 3(b)). Because of the very low light intensity and small radial angle range [~0°–45°] over which the intensity is integrated, the peak shape still remains highly asymmetric (figure 3(b)). Therefore, the Gaussian fit is not possible. The obtained diffraction angle (θd) values corresponding to the four diffraction rings are shown in the table 1.

The inter-planar spacing value (d_{hk}), as shown in table 1, is determined by using equation (4) and the reflection angle (θ), which is equal to the diffraction angle (θd) of the corresponding ring for a 2D crystal. For a 2D hexagonal lattice, also known as the triangular lattice, the inter-planar spacing (d_{hk}) as a function of Miller indices (hk) and primitive lattice vector a is given by [49]

\[
\frac{1}{d_{hk}} = \frac{4}{3} \left( h^2 + hk + k^2 a^2 \right)
\]  

(9)

If the assumed crystal lattice structure (2D hexagonal) and the Miller indices (hk) are correct, then all the d_{hk} values corresponding to each diffraction ring should produce the same value of a, on using equation (9). In this regard, nearly the same value of a is obtained on considering the two most basic 2D hexagonal Miller planes, (10) and (11) for the 1st and 2nd rings, respectively.

Therefore, 2D hexagonal ordering is still present along the two directions perpendicular to the applied field direction, for \( L = 80 \mu m \), as observed earlier for very short path length (\( L \leq 10 \mu m \)) [34]. Similar analysis, carried out for the 3rd and 4th rings, on considering the next most probable 2D hexagonal crystal Miller planes, (20) and (21), respectively, gives different values of a, as shown in table 1. In fact, no other Miller planes could be found to produce the same value of a for the d_{hk} values corresponding to the 3rd and 4th rings. Moreover, the measured diffraction angle values (θd) do not match with any other 2D crystal lattice structures, including the square and rectangular. This clearly indicates that the magnetic field induced crystal lattice is not 2D hexagonal.

### 3.4.3. Field induced crystal structure analysis on considering 3D hexagonal crystal

As the 3rd and 4th rings must be due to the structural periodicity along the 3rd dimension, i.e. the applied field direction, the possibility of a three dimensional (3D) crystal structure is present. Such a 3D hexagonal field induced crystal structure is observed in a magnetic nanofluid with long path length (\( L = 0.5 \) mm) and a larger size (>100 nm) core–shell nanoparticles [21]. Therefore, for \( L = 80 \mu m \), we consider the possibility of the formation of a 3D hexagonal crystal where the field induced columns occupy the vertices of the crystal lattice, as shown in figure 4.

A 3D hexagonal crystal acts as a 3D diffraction grating and obeys Bragg’s law [49]

\[
2d_{hkl} \sin \theta = n\lambda
\]  

(10)

where \( d_{hkl} \) is the spacing between the parallel lattice planes i.e., Miller indices (hkl) and θ is the angle between the incident light and the lattice planes. However, for a 3D crystal, the relation between diffraction angle θd and the reflection angle θ is \( \theta_d = 2\theta \). The inter-planar spacing \( d_{hkl} \) for a 3D hexagonal lattice is given by [49]
Table 2. Diffraction ring pattern analysis on considering 3D hexagonal crystal ordering.

| Ring number | Miller planes (hkl) | Miller-Bravais planes (hkil) | Planes of a form \{hkil\} | Primitive lattice vector |
|-------------|---------------------|-------------------------------|---------------------------|-------------------------|
| 1st         | (100), (010), (110) | (010), (110)                  | \{101\}                  | 7.347                   |
| 2nd         | (110), (210), (120) | (110), (210), (210)          | \{110\}                  | 7.289                   |
| 3rd         | (201), (021), (221), (201), (221), (021) | (201), (021), (221), (201), (221), (021) | \{201\} | 7.318 (Average of the values of \(a\) of 1st and 2nd rings) | 5.281 (Obtained by using \(a = 7.318\) µm) |
| 4th         | (211), (131), (211), (131), (211), (131), (211), (131) | (211), (131), (211), (131), (211), (131), (211), (131) | \{213\} | 7.421 (Obtained by using \(c = 5.281\) µm) |

\[
\frac{1}{d^2_{hkh}} = \frac{4}{3} \left( \frac{h^2 + h k + k^2}{a^2} \right) + \frac{l^2}{c^2} \tag{11}
\]

Here, \(a\) and \(c\) are the primitive lattice vectors. Physically, the primitive lattice vector \(a\) signifies the lateral spacing among the columns, i.e. structural periodicity along the two directions perpendicular to the applied field; while \(c\) signifies longitudinal spacing among the arrays of columns, which in other words is the longitudinal spacing among the columns formed along the applied field direction, as shown in figure 4. The 1st and 2nd rings are assumed to be due to diffraction from the two most basic 3D hexagonal Miller planes, \((100)\) and \((110)\), and their corresponding equivalent planes, which are related by crystal symmetry. The value of the primitive lattice vector \(a\) is found to be nearly the same for the 1st and 2nd rings, on using the equations (\((10)\) and \((11)\)), as given in table 2. The 3rd and 4th rings are assumed to be due to diffraction from the next most probable higher order Miller planes, \((201)\) and \((211)\), respectively. The value of lattice vector \(c\) is obtained by analyzing the 3rd ring (table 2), by using the average of the values of \(a\) as obtained from the 1st and 2nd rings and the equations (\((10)\) and \((11)\)). Now, by using this value of \(c\) (3rd ring), the value of lattice vector \(a\) is obtained for the 4th ring.
Interestingly, this value of $a$ (4th ring) is found to be nearly the same as the average of the values of $a$, as obtained from 1st and 2nd rings. This observation of the nearly same values of the primitive lattice vectors ($a$ and $c$), for all the four diffraction rings, further strengthens our argument of the formation of a 3D hexagonal lattice. The value of $c$ (=5.28 $\mu$m) and the average of the values of $a$ (=7.34 $\mu$m) for all the four diffraction rings are the average linear and lateral spacing values among the field induced columns, as shown in figure 4.

The Miller planes corresponding to each diffraction ring appear dissimilar, despite being crystallographically equivalent due to structural symmetry, as shown in table 2. In order to address this issue, the Miller–Bravais ($\{hkil\}$) indexing is usually used for 3D hexagonal crystal, where a crystallographic plane is expressed in the form of four basic vectors $a_1$, $a_2$, $a_3$, and $c$, as shown in figure 5. The index $i$ is the reciprocal of the fractional intercept on the $a_i$ axis. The value of $i$ depends on the values of $h$ and $k$ by the following relation $h + k = -i$ [49]. The advantage of using ($hkil$) representation is that it can give similar indices to similar planes. The equivalent planes, which are related by symmetry are called planes of a form, and when enclosed in braces ($\{hkil\}$), stands for the whole set, as given in table 2. One representative Miller–Bravais plane ($hkil$) corresponding to each diffraction ring is shown in the schematic of 3D hexagonal lattice in figure 5 for the visualization purpose.

**3.4.4. Mechanism of the path length dependent field induced crystal ordering in magnetic nanofluid**

On applying magnetic field ($H_a$) in magnetic nanofluid, the coupling constant ($\Lambda$) among the magnetic nanoparticles increases (equation (3)), due to the increase in magnetic dipolar interaction energy ($U_{ij}$) (equation (2)). This leads to the formation of linear chains along the direction of applied field. On increasing the field strength ($H_a$), the chains of nanoparticles undergo aggregation, lateral to the direction of the applied field, known as zippering aggregation, thereby forming columns of laterally zipped chains [30]. The zippering aggregation is shown (figures 2(f) and (g)) for ferrofluid emulsion, another magnetic dipolar system, but with larger size of the dispersed phase, magnetic nanoparticle containing oil droplets (size $\sim 200$ nm) dispersed in water, which makes it easier for visualization of the zippering aggregation process under phase-contrast optical microscope. For magnetic nanofluid, the origin of this zippering aggregation is attributed to the thermal fluctuation induced short range attraction among the nanoparticle chains and the requirement to minimize the total dipolar potential energy of the system [30]. For magnetic nanofluid, the summation of dipolar interaction energies, among all the particles constituting different columns (in place of the columns, chains are shown in figure 6 for better visualization), gives the total potential energy ($U_{total}$ shown in figure 6) of the system under the applied field ($H_a$). However, the main contribution to the total potential energy comes from the dipolar interactions among the nanoparticles constituting the nearest neighbor columns (chains in figure 6(b)), as the dipolar interaction strength decreases rapidly with increasing inter-particle distance ($r_{ij}$) (equation (2) and figure 6(a)). Therefore, for a given volume of magnetic nanofluid, the total potential energy ($U_{total}$) of the system can be minimized by choosing a crystal ordering of columns such that ($a$) maximizes the inter-column spacing, therefore, the inter-particle distance ($r_{ij}$) and/or ($b$) maximizes the possibility of $\theta_{ij} \approx 90^\circ$, which results in negative values of $U_{ij}$, therefore, lowers the total potential energy ($U_{total}$) (equation (2) and figure 6(b)).

**3.4.5. 2D hexagonal crystal ordering for short path length**

For shorter path length, e.g. $L \leqslant 10$ $\mu$m, the 2D hexagonal periodic spacing among the columns lateral to the applied field direction maximizes the inter-column spacing (condition (a) as discussed above) and hence
minimizes the system potential energy (equation (2)) [34]. Moreover, on increasing the column widths by zippering aggregation of the chains due to increased field strength ($H_o$), the columns becomes more rigid, which leads to the dominance of long range end pole repulsion among the columns over the short-range thermal fluctuation induced attraction of the chains of nanoparticles [35]. Therefore, in order to maximize the inter-column spacing and due to the end pole repulsions among the rigid columns, 2D hexagonal crystal structure is formed for the short path lengths of magnetic nanofluid under applied field [34].

3.4.6. 3D hexagonal crystal ordering for long path length
Simultaneous increase in column length, with the increase in path length, also increases the number of particles with $\theta_{ij} = 90^\circ$ ($U_{ij} = +ve$, as per equation (2)), known as the in-registry positions (particles 1 and 2 in figure 6(b)) for two neighboring columns, which again results in the increase in the potential energy of the system ($U_{Total}$) [30]. Therefore, for the longer sample path length ($L = 80 \ \mu m$), 2D hexagonal lattice ordering is avoided by the formation of 3D hexagonal structure; where the column lengths are shorter and has a lower system potential energy due to the reasons discussed below. For a given nanofluid volume with longer path length ($L = 80 \ \mu m$), shorter lengths of the column and their spatial ordering in 3D hexagonal lattice leads to—
(a) significant increase in the number of nanoparticles with $\theta_{ij}$ approaching $0^\circ$ or $180^\circ$ among the neighboring columns (figure 6(b)),
(b) simultaneous decrease in the number of particles with $\theta_{ij} (=90^\circ)$, and
(c) decrease in the inter-column spacing ($r_{ij}$). In fact, in magnetic nanofluid, the experimental observation of the formation of columns with shorter lengths is also reported earlier [55]. The above mentioned factors (a) and (b) dominate over factor (c) in making the dipolar interaction energy ($U_{ij}$) negative (equation (2) and figure 6(b)); this leads to the decrease in the total potential energy ($U_{Total}$) of the system. This is the reason why the magnetic field induced crystal ordering in magnetic nanofluid, formed by the spacing of columns, undergoes a transition from 2D hexagonal to 3D hexagonal on increasing the path length from $L \leq 10 \ \mu m$ to $L = 80 \ \mu m$ [22, 34].

Figure 6. Schematic to describe the magnetic dipolar interaction energy among magnetic nanoparticles from (a) two neighboring chains, and (b) neighboring columns (chains are shown in place of columns for clarity in visualization) located at the vertices of a 3D hexagonal crystal ordering, which is a favorable structural configuration to decrease the total dipolar potential energy, due to more number of possible negative dipolar interaction energies among the nanoparticles.
3.4.7. Role of field strength \((H_0)\) on the 3D crystal structure in magnetic nanofluid

As discussed in the previous section 3.4.4, on increasing the field strength \((H_0)\) to an intermediate value, zipper aggregation of the chains take place leading to the formation of columns, which then undergoes crystal ordering, 2D hexagonal or 3D hexagonal, depending on the path length \((L)\). Further increase in field strength \((H_0)\) dictates the degree of ordering of the already formed crystal, 3D hexagonal in our case \((L = 80 \ \mu\text{m})\). The applied magnetic field strength \((H_0)\) is 300 G, beyond which it is not possible to increase in this experiment, due to the overheating of the solenoid. The intermediate field strength \((H_0)\) has the following implications on the crystal ordering: (a) the end-pole repulsion among the columns are weak [35], which results in significant thermal fluctuations of the field induced columns located at the vertices of the 3D crystal lattice (figures 4 and 6) [30, 52], (b) the crystal structure is polycrystalline, i.e. a large number of single crystals are randomly oriented to each other, which is confirmed by the continuous circular diffraction ring circumference (figure 1(b)), rather than diffraction spots. If the applied field strength is significantly increased \((H_0 \gg 300 \ \text{G})\), it—a increases the rigidity of the columns at the lattice vertices, since thermal fluctuations get decreased, due to the increased end-pole repulsion among the columns, and (b) decreases the degree of polycrystallinity of the crystal structure. Therefore, once the 3D hexagonal crystal structure is formed at intermediate field strength \((H_0 \sim 300 \ \text{G})\) in this case, further increase in magnetic field strength \((H_0 \gg 300 \ \text{G})\) does not affect the crystal lattice spacing, the values of primitive lattice parameters \((a\) and \(c)\) remain same; however, the columns occupying the lattice vertices become more rigid (figure 4) and degree of polycrystallinity of the crystal structure also decreases.

3.5. Crystal disorder of first type and its implication—photonic glass integrated with photonic crystal

The thermal fluctuation of the field induced columns contributes to the crystal disorder of the first type, which is a short range disorder and manifests in the diffraction pattern as the diffuse scattering background, as observed in figure 1(b) [30, 51–53, 56]. Although in many colloidal crystals, inherent colloidal size polydispersity also contribute to the disorder of first type [57, 58]; the magnetic nanoparticles constituting the field induced columns in this experiment are highly monodisperse (polydispersity index, PDI \(\sim 0.092\)), therefore, does not contribute to the crystal disorder. The presence of crystal disorder makes the field induced structural configuration inside the magnetic nanofluid mimic a photonic glass integrated with a 3D photonic crystal [19, 40, 50, 59, 60]. Photonic glass, a medium containing a completely disordered arrangement of monodisperse colloids and characterized by the speckle pattern, showed random lasing originating from multiple scattering [19]. In photonic glasses, the Mie resonances originating from the constituting colloidal particle (field induced columns in this case) size (column size \(\sim \text{visible light wavelength}\)) and the high refractive index (RI) contrast of magnetic nanoparticles \((\text{Fe}_3\text{O}_4 \text{RI} \sim 2.42)\), constituting the columns, with the carrier liquid (kerosene \(\text{RI} \sim 1.44\)) induces weak localization of light and therefore, influences the light transport behavior [31, 38]. Fano resonance, originating from the interference of multiple scattering light pathways between the Mie and Bragg scattered lights, is theoretically shown to govern the light transport for a photonic crystal with a certain degree of structural disorder [61, 62]. Simultaneous presence of both structural order and disorder in the same system also gives rise to both light localization and Fano resonance in magnetic nanofluids [38, 41]. Our finding of photonic glass property with 3D photonic crystalline behavior of magnetic nanofluid under applied magnetic field supports the recent theoretical finding that Fano resonance and light localization of the same physical origin, which results from the interference among different scattering paths arising from the multiple light scattering by the structural disorder [38, 41, 62].

3.6. Reason for broad width of the diffraction rings—small crystal size

In the case of atomic or molecular crystals of solid state systems, when the degree of crystal ordering is excellent, sharp diffraction rings, known as Debye–Scherrer rings are observed in Debye–Scherrer x-ray powder diffraction method [49]. On the introduction of crystal disorder, e.g. for the nanocrystalline-glass structure, electron diffraction rings with broad widths are observed [63]. Introduction of the crystal disorder of the second type, also known as the cumulative disorder, leads to diffraction ring width (peak) broadening, which increases with increase in diffraction order [51, 56, 57, 64]. However, as shown in the figure 3, the diffraction ring widths do not increase with the increase in diffraction order, therefore, the broad diffraction peaks are not caused by the crystal disorder of second type. Moreover, the diffraction ring (peak) widths still remained broad, even after the subtraction of the diffuse scattering background from the diffraction pattern, as shown in figure 3. This observation confirms that the crystal disorder of first type, originating from the thermal fluctuation of the field induced columns at the lattice vertices, did not play any role in broadening the ring width; only decreased the peak intensity and redistributed it as the diffuse scattering background [30, 51–53].

The formation of continuous circular ring circumference, rather than diffraction spots, confirm the following: (a) the field induced crystal structure is polycrystalline, i.e. a large number of single crystals are randomly oriented to each other and (b) the crystals are smaller in size, as the diffraction volume inside the
nanofluid is small (cylindrical volume $\sim 0.0157 \text{ mm}^3$, beam width $\sim 0.5 \text{ mm}$ (cylinder diameter), path length $\sim 80 \mu m$ (cylinder length)), whereas the values of the primitive lattice vectors are significantly large ($a \sim 7.344 \mu m$ and $c \sim 5.281 \mu m$) [49]. If the crystals are smaller in size, the number of parallel lattice (Miller) planes is too small for a sharp diffraction maximum (peak) to build up, i.e. widths in the diffraction ring pattern become broadened; the additional ring broadening introduced by small crystal size is also independent of the diffraction order [51, 37]. Therefore, the diffraction order independent broadening of the diffraction ring width, as observed in figures (1(b) and 3(b)) is due to small crystal size. In fact, small crystallites separated by grain boundaries are also the cause for the broad widths of the chromatic diffraction rings, formed by the interaction of white light with the field induced 2D hexagonal crystal structure of magnetic nanofluid, for very short path length ($L = 10 \mu m$) [23, 34, 35].

4. Conclusions

We demonstrated that the path length ($L$) dictates the light–matter interaction (diffraction or scattering pattern) in a stable colloidal suspension of magnetic nanoparticles, known as the magnetic nanofluid, under applied magnetic field. We observed a single corona like light scattered ring for the longer path length ($L = 1 \text{ mm}$), due to the scattering of light from the surface of cylindrical columns of nanoparticle aggregates formed along the applied field direction; whereas we observed concentric diffraction ring pattern for shorter path length ($L = 80 \mu m$), as the condition for maintaining temporal coherence, therefore, the constructive interference is satisfied. The analysis of the diffraction rings suggests the formation of 3D hexagonal crystal structure inside the magnetic nanofluid under applied field, which confirms that the transformation of the field induced crystal structure from 2D hexagonal to 3D hexagonal takes place in the range $10 \mu m < L < 80 \mu m$; therefore, explains the path length dependent field induced crystal ordering inside magnetic nanofluid [22, 34]. The spacing between the field induced columns in the lateral and longitudinal directions are found to be 7.344 $\mu m$ and 5.281 $\mu m$, respectively. To the best of our knowledge, this is the first experimental observation of a 3D colloidal crystal, which is formed by the non-contact spatial ordering of columns of aggregated nanoparticles, not by the packing of particles; thereby making the crystal periodicity much larger than the individual colloidal particle diameter [13, 65]. Moreover, the observation of diffuse scattering background and speckles within the diffraction ring pattern confirm the presence of certain degree of crystal disorder of first type embedded within the 3D crystal structure, originating from thermal fluctuation of field induced columns at the lattice vertices [30, 51, 52, 56, 57]. This makes the field induced structure photonic glass integrated with photonic crystal; where the degree of ordering can be tuned by controlling the applied magnetic field strength, nanoparticle size and particle volume fraction. Our results showing the ability to reversibly tune and simultaneously harness the degree of both the structural disorder and order in magnetic nanofluid based photonic materials using an external stimulus, such as magnetic field, opens up the possibility to develop new generation of tunable photonic devices, e.g. tunable random lasers [16, 19, 66].

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