Effect of Nanoparticle Aggregation on Thermal and Rheological Properties of Nanofluids

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4.1 Introduction

Preparation of stable nanofluids is the key issue of nanofluid research and application. Nanoparticles can exist in several configurations ranging from a well-dispersed mode to totally agglomerated state. The stability of nanofluids can be classified into three categories: (i) Kinetic stability: Nanoparticles dispersed in the nanofluids are under Brownian motion which can overcome their sedimentation caused by gravitational force; (ii) Dispersion stability: Due to the aggregation of nanoparticles, the dispersion of nanoparticles in fluids may deteriorate with time; and (iii) Chemical stability: No chemical reactions between the suspended nanoparticles or between the base fluid and nanoparticles are desired in nanofluids. Therefore, nanofluids are to be carefully prepared to ensure their long term stability.

In stationary state, the sedimentation velocity of small spherical particles in a liquid follows the Stokes law:

\[
V = \frac{2d^2}{9\eta} (\rho_p - \rho_f) g
\]

where ‘V’ is the sedimentation velocity of particles, ‘d’ is the size of particles, \( \eta \) is the viscosity of the liquid medium, ‘g’ is the gravitational acceleration, \( \rho_p \) and \( \rho_f \) are the density of the particles and the liquid medium respectively. This equation reflects a balance of the gravity, buoyant force and frictional force that are acting on the suspended nanoparticles. According to Eq. (4.1), to reduce the sedimentation velocity of nanoparticles and to produce stable nanofluids,
one should reduce the size of nanoparticle and increase the base fluid viscosity or minimize the density difference between the nanoparticles and the base fluid. Among the above, reducing the particle size should remarkably decrease the sedimentation velocity of the nanoparticles and improve the stability of nanofluids. However, the smaller nanoparticles have higher surface energy, thereby increases the possibility of aggregation of nanoparticles. Therefore, the key to prepare stable nanofluids is to use smaller nanoparticles and to prevent the aggregation of the small nanoparticles by proper surface stabilization.

In majority of nanofluid studies, nanoparticles are produced from dry powder and then dispersing in base fluids with the help of added dispersants or by pH adjustment of the base fluid. The dispersion is usually prepared under mechanical stirring, ultrasonic bath, ultrasonic disruptor or high-pressure homogenizer with the help of added dispersants or by pH adjustment of the base fluid. The effect of ultrasonication and mechanical stirring is to break down the aggregates of the nanoparticles. The dispersant addition and pH adjustment is to prevent the reaggregation of nanoparticles thereby producing stable nanofluids. Among the different dispersion techniques, ultrasonication is a simple and well accepted technique for the production of well dispersed nanofluids.

DLS, rheology and microscopy studies are often used to probe the stability and aggregation effects in nanofluids. There are many studies on aggregation in nanofluids using DLS. Viscosity ($\eta$) measurements are also used to probe the aggregation kinetics in nanofluids. The mean number of nanoparticles within the aggregates depends on the hydrodynamic interactions and there will be an enhancement of viscosity with increasing volume concentration of particles or aggregates. Microscopy is another powerful tool to
examine the aggregation in nanofluid. Some of the previous reports show direct evidence for nanofluid aggregation using microscopy studies.\textsuperscript{[138, 152, 155, 157]}

Improved dispersion stability with least enhancement in $\eta$ is inevitable for the practical applications of nanofluids. However, in most experimentally tested nanofluids, there is a competition between the growth of fractal-like structures, coalescence into large clumps, sedimentation and fragmentation. To have a better understanding on $k$ enhancements, one should use model nanofluids with long term stability. Towards this goal, both stable and aggregating nanofluids with particle size less than 10 nm are synthesized for the present study and $k$ is measured as function of $\phi$. Even if there are many studies on effect of aggregation on $k$ of nanofluids, a systematic $k$ study together with rheology, DLS and microscopy is still lacking, which is yet another objective of the present study. We follow the time dependant $k$, average particle size, microstructure and $\eta$ of a stable and aggregating nanofluid after sonication.

4.2 Effect of Volume Fraction on Thermal Conductivity of Stable and Aggregating Nanofluids

In the present study, $k$ is measured as a function of $\phi$ for both stable and unstable nanofluids. Stable oil based nanofluids are prepared by dispersing oleic acid coated $\text{Fe}_3\text{O}_4$ nanoparticles in kerosene and hexadecane. These nanofluids are perfectly stable with no aggregation due to steric stabilization offered by oleic acid. The DLS, rheology and microscopy studies confirm the absence of aggregation in the above nanofluids. The particle size measured by DLS matches with the primary crystallite size obtained from XRD results indicates the absence of aggregation of nanoparticles in suspensions. Moreover, rheology studies in these nanofluids show a
Newtonian behavior and the microscopy images show no aggregates (with size > 200 nm). Figure 4.1(a) shows the variation of $k/k_f$ ($k_f$ being the base fluid thermal conductivity) and the percentage of $k$ enhancement as a function of $\phi$ for kerosene based Fe$_3$O$_4$ nanofluids together with Maxwell’s lower fit. Only moderate $k$ enhancement within the predictions of EMT is observed here. The maximum $k$ enhancement observed is 23% for nanofluid with $\phi=0.078$. The data fitted with Maxwell model show good agreement especially at higher volume fractions. The enhancement above $\phi=0.0176$ could be due to small clusters (dimmers or trimmers) formed in the nanofluid due to magnetic dipolar attractions. It appears that the wetting of nanoparticles is enhanced due to the organic sheath, which in turn leads to a lower interfacial thermal resistance. We find that nanofluids with very small particles (~ 5 nm) are also prone to settling when particles are uncoated. The stable hexadecane based Fe$_3$O$_4$ nanofluids also exhibit similar $k$ variations within the predications of EMT. Moderate $k$ enhancement within the predictions of EMT is observed for TMAOH coated stable water based Fe$_3$O$_4$ nanofluids [Fig. 4.1 (b)]. The maximum $k$ enhancement observed is 9% for nanofluid with $\phi=0.038$. The electrostatic stabilization offered by TMAOH render long term stability against aggregation to water based nanofluids. The moderate $k$ enhancement within the predictions of EMT observed for stable nanofluids in the present study is in agreement with the recent reports.$^{[60-62,69]}$

For a nanofluid containing non-interacting spherical nanoparticles, the EMT$^{[37]}$ predicts

$$
\frac{k}{k_f} = \frac{1+2\beta\phi}{1-\beta\phi}
$$

where $\phi$ is the nanofluid volume fraction; $k$ and $k_f$ are the thermal conductivities of the nanofluid and the base fluid respectively. $\beta$ is given by $(k_p-k_f)/(k_p+2k_f)$, where $k_p$ is the thermal conductivity of nanoparticle. When a finite temperature discontinuity exists at the
nanoparticle-fluid interface, \( k_f \rightarrow k_f + \alpha k_p \), where \( \alpha = 2R_b k_f / d \), \( R_b \) is the interfacial thermal resistance and ‘d’ is the nanoparticle size.

![Graph of \( k/k_f \) and percentage enhancement vs. volume fraction.](image)

**Fig. 4.1:** The variation of \( k/k_f \) and the percentage (\%) of \( k \) enhancement as a function of \( \phi \) (a): For kerosene based and (b): For water based Fe\(_3\)O\(_4\) nanofluids together with Maxwell’s lower fit using \( k/k_f = 1+3\phi \).

CuO nanofluids are prepared by dispersing uncoated CuO nanoparticles in EG. The lack of surface functionalization leads to aggregation in the above nanofluids, which is evident in DLS, rheology and microscopy results. The particle size measured by DLS is much higher than the crystallite size obtained from XRD results that confirm the aggregation of nanoparticles in
suspensions. Moreover, rheology studies show a shear thinning behavior with enhanced zero shear η values and the microscopy images confirm the presence aggregates in the above nanofluids. Figure 4.2 shows the variation of k/k_f and % of k enhancement as a function of φ for EG based CuO nanofluids together with Maxwell’s lower fit. Here, the enhancement in k/k_f is much above the EMT predictions. Maximum k enhancement observed is 13% for a nanofluid with φ=0.0131. Water based aggregating CuO nanofluids also shows k enhancement beyond EMT predictions. Similar enhancement in k is reported in aggregating nanofluids.⁵⁹, ⁶¹, ¹³⁸, ²⁷⁶

![Graph showing the variation of k/k_f and % of k enhancement as a function of φ for EG based CuO nanofluids together with Maxwell’s lower fit.](image)

Fig. 4.2: The variation of k/k_f and % of k enhancement as a function of φ for EG based CuO nanofluids together with Maxwell’s lower fit using k/k_f=1+3φ.

The present results unambiguously confirm the prominent role of agglomeration on thermal properties of nanofluids and the importance of surface functionalization of nanoparticles for improved stability.
4.3 Effect of Aggregation on Thermal and Rheological Properties of Nanofluids

Ultrasonication is often used to improve the dispersion stability of nanofluids.\textsuperscript{[39, 102, 103, 114, 121-124, 128, 138, 277, 278]} The cluster size of EG based iron (Fe) nanofluids are found to decrease with the increase in ultrasonication duration.\textsuperscript{[39, 128]} In a recent study, it is shown that the size of agglomerated particles and number of primary particles in a cluster is significantly decreased with elapsed ultrasonication time in alumina and copper oxide nanofluids.\textsuperscript{[124]} In an ultrasonic system, the tip of a horn is driven at ultrasonic frequencies by piezo transducers to induce oscillations (typically 20–50 kHz). Energy is transferred into the fluid in the form of pressure waves that induce cavitations that is subsequently forced to collapse, and releases intense pressure waves into the fluid. Particles adjacent to the cavity are subjected to normal and shear forces which can cause breakage of particle if they are of sufficient intensity.\textsuperscript{[279]} In the present study, the effects of ultrasonication and subsequent aggregation on thermal and rheological properties of various nanofluids are investigated together with DLS and microscopy studies.

4.3.1 Kerosene Based Magnetite Nanofluids

The nanofluids are sonicated for 30 minutes at a power of 20 W using an ultrasonicator horn and $k$ is monitored as a function of time, ten minutes after the sonication is stopped. Figure 4.3 shows the variation in $k/k_f$ and the $k$ enhancement with time for kerosene based $\text{Fe}_3\text{O}_4$ nanofluids at three different volume fractions $\phi=0.0171, 0.050$, and $0.082$. It can be seen that the $k_c$ values are time independent, though the particle number density is much high. Moreover, the observed $k$ enhancement with $\phi$ is within the limits of EMT.
Fig. 4.3: The variation of $k/k_f$ and % of $k$ enhancement with time after sonication for kerosene based Fe$_3$O$_4$ nanofluids with $\phi=0.0171$, 0.050 and 0.082.

DLS studies confirm the absence of aggregation in the above nanofluids due to steric stabilization of nanoparticles. Figures 4.4 (a), (b) and (c) shows the mean number percentage as a function of particles size at different time intervals after sonication of 5, 20, 40, and 60 minutes, for kerosene based Fe$_3$O$_4$ nanofluids at different particle loading of $\phi=0.082$, 0.05 and 0.0171 respectively. An invariant average particle size with time is observed, which is consistent with the primary crystallite size obtained from XRD results.

Rheological studies also support the absence of aggregation in properly functionalized Fe$_3$O$_4$ nanofluids. Figure 4.5 shows the variation in $\eta/\eta_0$ ($\eta_0$ being the base fluid viscosity) and the $\eta$ enhancement with elapsed time, after sonication, for kerosene based Fe$_3$O$_4$ nanofluids at three different volume fractions of $\phi=0.0171$, 0.050, and 0.082. The viscosity ratio does not show
any variation with time. Moreover, the flow curves show Newtonian behavior with less $\eta$ enhancement, a characteristic of well dispersed nanofluids.

![Graph showing the variation of nanoparticles size with time](image)

**Fig. 4.4 (a), (b) and (c):** The plot of mean number percentage as a function of particles size at different time intervals after sonication of 5, 20, 40, and 60 minutes for kerosene based Fe$_3$O$_4$ nanofluids with $\phi=0.082$, 0.05 and 0.0171 respectively. (d), (e) and (f) shows the variation of average particle size with time for kerosene based Fe$_3$O$_4$ nanofluids with $\phi=0.082$, 0.05 and 0.0171 respectively.

Finally, the stability of surface functionalized Fe$_3$O$_4$ nanofluids is confirmed by optical microscopy studies. Figures 4.6 (a–c) shows the micrograph of kerosene based Fe$_3$O$_4$ nanofluid with a particle loading of $\phi=0.050$ at three different time intervals (t=5, 30, and 60 minutes) after sonication. The Fe$_3$O$_4$ nanofluid micrographs show no aggregation (with cluster size > 200 nm) with elapsed time after sonication, due to sufficient repulsion through steric hindrance.
Fig. 4.5: The variation in $\eta / \eta_0$ and the percentage of enhancement of $\eta$ with time after sonication for kerosene based Fe$_3$O$_4$ nanofluids with $\phi = 0.082$, 0.05 and 0.0171.

Fig. 4.6 (a), (b) and (c): The phase contrast microscopy images taken immediately after sonication, after 30 and 60 minutes of sonication for Fe$_3$O$_4$ nanofluids with $\phi = 0.05$
4.3.2 Hexadecane and Water Based Magnetite Nanofluids

k is measured as a function of time after sonication for stable hexadecane and water based Fe$_3$O$_4$ nanofluids.

![Graph showing the variation of k/k$_f$ and % of k enhancement with time after sonication for (a): Hexadecane based Fe$_3$O$_4$ nanofluids with $\phi=0.0164$ and 0.0608. (b): Water based Fe$_3$O$_4$ nanofluids with $\phi=0.0102$ and 0.0213.]

Figure 4.7 (a) shows the variation of k/k$_f$ and % of k enhancement with time after sonication for hexadecane based Fe$_3$O$_4$ nanofluids with $\phi=0.0164$ and 0.0608. Fig. 4.7 (b) shows the variation of k/k$_f$ and % of k enhancement with time after sonication for TMAOH coated water based
Fe₃O₄ nanofluids with $\phi=0.0102$ and 0.0213. Time independent k is observed in both the cases after sonication. Oleic acid and TMAOH coating renders steric and electrostatic stabilization respectively to hexadecane and water based Fe₃O₄ nanofluids.

DLS studies confirm the absence of aggregation in the above nanofluids. Both hexadecane [Fig. 4.8 (a)] and water based [Fig. 4.8 (b)] Fe₃O₄ nanofluids show an invariant particle size distribution with time, after sonication. Moreover, the average particle size measured using DLS matches with the primary crystallite size obtained from XRD results in both the cases.

Fig. 4.8: The plot of mean number percentage as a function of particles size at different time intervals after sonication of 5 and 60 minutes for (a): Hexadecane based Fe₃O₄ nanofluids with $\phi=0.0608$. (b): Water based Fe₃O₄ nanofluids with $\phi=0.0213$. 
η studies confirm the long term stability of surface functionalized hexadecane and water based Fe$_3$O$_4$ nanofluids. An invariant η with time after sonication is observed in both water based [Fig. 4.9 (a)] and hexadecane based [Fig. 4.9 (b)] Fe$_3$O$_4$ nanofluids. Moreover, the flow curves show a Newtonian behavior with least enhancement in η. Finally, the absence of aggregation in the above nanofluids is corroborated by microscopy studies which show no aggregation of particles with elapsed time after sonication.

![Graph](image)

Fig. 4.9: The variation in η/η$_0$ and the percentage of enhancement of η with time after sonication for (a): Water based Fe$_3$O$_4$ nanofluids with φ=0.0213 and (b): Hexadecane based Fe$_3$O$_4$ nanofluids with φ=0.0608.

### 4.3.3 Hexadecane Based Silver Nanofluids

k is measured as a function of time, after sonication, for Ag nanofluids. Figure 4.10 shows the variation of k/k$_f$ and % of k enhancement with time after sonication for hexadecane based Ag nanofluids with φ=0.0116. An invariant k is observed with elapsed time after sonication. Here,
the Ag nanoparticles are stabilized by oleylamine surfactant. The amine group of oleylamine binds to the surface of the silver, and the aliphatic chain extends into the nonpolar solvent, preventing aggregation of particles due to steric hindrance. DLS studies (Fig. 4.11) show an invariant particle size distribution (in agreement with XRD results) with time, after sonication, in these nanofluids.

![Graph](image)

**Fig. 4.10:** The variation of $k/k_f$ and % of $k$ enhancement with time after sonication for hexadecane based Ag nanofluids with $\phi=0.0116$.

Fig. 4.12 shows the variation in $\eta/\eta_0$ and the percentage of enhancement of $\eta$ with time after sonication for hexadecane based Ag nanofluids with $\phi=0.0116$. An invariant $\eta$ ratio observed with elapsed time after sonication, confirms the absence of aggregation in the Ag nanofluids.
Fig. 4.11: The plot of mean number percentage as a function of particles size at different time intervals after sonication of 5, 20, 40 and 60 minutes for hexadecane based Ag nanofluids with $\phi=0.0116$.

Fig. 4.12: The variation in $\eta/\eta_0$ and the percentage of enhancement of $\eta$ with time after sonication for hexadecane based Ag nanofluids with $\phi=0.0116$. 
UV-Vis spectroscopy is often used to detect aggregation in metal nanoparticles. This method relies on the fact that the plasmon band, characteristic of small nanoparticles, is red-shifted and broadened when nanoparticles come into close contact.\textsuperscript{[280]} In the present study, Ag nanofluids show intense surface plasmon resonance absorption (SPR) at 400 nm. Figure 4.13 shows the UV Visible spectra of Ag nanofluids with varying Ag nanoparticle concentrations. No shift in SPR with increasing Ag nanoparticle concentration (from $\phi=0.00001$ to $\phi=0.0001$) is observed. Moreover, no shift in SPR is observed with time after sonication (Fig. 4.13 inset). This indicates the absence of aggregation in the above nanofluids. Microscopy images also show no aggregation with elapsed time.

![Image of UV-Visible spectra](image)

Fig. 4.13: The UV Visible spectra of Ag nanofluids with varying Ag nanoparticle concentrations (from $\phi=0.00001$ to $\phi=0.0001$). Inset shows the UV visible spectra of silver nanofluids after 5 and 60 minutes of sonication.
4.3.4 Ethylene Glycol Based Copper Oxide Nanofluids

$k$ is measured as a function of time after sonication in EG based CuO nanofluids. Here, the sonication time and power (20 W) are exactly the same as in the case of Fe$_3$O$_4$ nanofluid. Figure 4.14 shows the variation of $k/k_f$ and the $k$ enhancement with time, after 30 minutes of sonication for EG based CuO nanofluids of four different particle concentrations of $\phi = 0.0018$, 0.0054, 0.0092, and 0.0131. Here, the highest value of $k/k_f$ is observed immediately after sonication. The $k/k_f$ decreases with elapsed time and finally reaches an equilibrium value after a time interval of about 45 minutes. A systematic increase in $k/k_f$ with particle loading is observed. The peak enhancement in $k$ at $\phi=0.0131$ is $\sim 14\%$. A similar effect of aggregation on thermal conductivity is observed for water and EG based Cu nanofluids earlier.[138]

![Graph showing the variation of $k/k_f$ and % of $k$ enhancement with time after sonication for ethylene glycol based CuO nanofluids with $\phi=0.0018, 0.0054, 0.0092, and 0.0131$.](image)

Fig. 4.14: The variation of $k/k_f$ and % of $k$ enhancement with time after sonication for ethylene glycol based CuO nanofluids with $\phi=0.0018, 0.0054, 0.0092, and 0.0131$.  

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In aggregating CuO nanofluids, the ultrasonication leads to disintegration of larger nanoparticle clusters into smaller ones. Due to the absence of stabilizers, once the sonication is stopped, the small nanoparticle clusters reaggregate and form bigger clusters that are subsequently settled. This leads to a decrease in k with elapsed time after sonication. In recent reports, it is shown that the measurement of k, immediately after the ultrasonication, will result in unfinished micro-oscillations of nanoparticles and fluid molecules that can contribute to thermal energy transport, leading to higher k enhancement.\cite{86,109} If the above prediction is true, base fluid also should have exhibited a time dependent k variation after sonication. We have measured k of base fluids (kerosene, hexadecane, water and EG) as a function of time after sonication where we observe a time independent k. Sonication time and power is exactly the same as in the case of other nanofluids. These finding disprove the micro-oscillation concept.\cite{86,109}

To confirm the aggregation in CuO nanofluids, the cluster size is measured as a function of time after sonication. Figures 4.15 (a)-(d) shows the mean number percentage as a function of cluster size at different time intervals after sonication of 5, 20, 40, and 60 minutes for EG based CuO nanofluids of different particle loading $\phi=0.0131, \ 0.0092, \ 0.0054$ and $0.0018$ respectively. Figures 4.4 (e)-(h) shows the variation of average particle size with time for the above nanofluids. The average particle size is found to increase with time after sonication in CuO nanofluids. The average size of CuO nanoaggregates have grown from 23 to 95 nm for the lowest concentration, while its value exceeded 300 nm for nanofluid with $\phi=0.0131$. 
Fig. 4.15: (a), (b), (c) and (d): The plot of mean number percentage as a function of particles size at different time intervals after sonication of 5, 20, 40, and 60 minutes for ethylene glycol based CuO nanofluids with $\phi=0.0131$, 0.0092, 0.0054 and 0.0018 respectively. (e), (f), (g) and (h) shows the variation of average particle size with time for ethylene glycol based CuO nanofluids with $\phi=0.0131$, 0.0092, 0.0054 and 0.0018 respectively.

The additional evidence for aggregation in CuO nanofluids is obtained from the time dependent rheology studies after sonication. Figure 4.16 shows the variation in viscosity ratio ($\eta/\eta_0$) and the percentage of enhancement of $\eta$ with time for EG based CuO nanofluids at different particle loading of $\phi=0.0018$, 0.0054, 0.0092, and 0.0131. The $\eta$ ratio increases with time after
sonication in all the nanofluids. The nanofluid with lower particle loading shows least enhancement in $\eta$ with time and the extent of $\eta$ enhancement is higher for nanofluids with higher particle loading owing to the greater degree of aggregation. As aggregates are formed with time, interaction among nanoparticles increase and the flow resistance also increases, that leads to an increase in $\eta$.

![Graph showing variation in $\eta/\eta_0$ and percentage of enhancement of $\eta$ with time after sonication for ethylene glycol based CuO nanofluids with $\phi=0.0018, 0.0054, 0.0092, \text{and } 0.0131$.](image)

Fig. 4.16: The variation in $\eta/\eta_0$ and the percentage of enhancement of $\eta$ with time after sonication for ethylene glycol based CuO nanofluids with $\phi=0.0018, 0.0054, 0.0092, \text{and } 0.0131$.

Flow curves performed at different time intervals after sonication also confirm the progressive aggregation of particles in CuO nanofluids. Figure 4.17 shows the variation of $\eta$ with shear rate at different intervals after sonication for EG based CuO nanofluids with $\phi=0.0152$. A progressive increase in $\eta$ is observed with time. Moreover, a shear thinning behavior is observed for all time intervals.
The rapid increase of $\eta$ at low shear rate indicates the formation of an interacting network of aggregated nanoparticles. As the shear rate is increased, nanoparticle network is broken, leading to a decrease in $\eta$. Figure 4.17 inset shows the variation of $\eta/\eta_0$ with time after sonication for EG based CuO nanofluids with $\phi=0.0152$, at a shear rate of 50 s$^{-1}$. $\eta$ ratio increases linearly with time after sonication. Figure 4.18 shows the variation of $\eta$ with shear stress at different intervals after sonication for the above nanofluid. A progressive increase of the yield stress and shear-thickening is observed with time. The elapsed time and the concomitant yield stress push the onset of shear thickening to higher stress values. A similar enhancement in shear stress is reported in dielectric glass spheres in mineral oil and magnetite-filled polyethylene glycol (PEG) rods suspended in PEG recently.\textsuperscript{281}
Fig. 4.18: The variation of $\eta$ with shear stress at different time intervals after sonication for ethylene glycol based CuO nanofluids with $\phi=0.0152$.

To obtain macroscopic evidence of the aggregation process, the phase contrast microscopic images are taken at different time intervals. Figure 4.19 shows the microscopy images of CuO based nanofluids at three different time intervals (t=5, 30, and 60 minutes) after sonication for different $\phi$ values of 0.0054 (a1–a3), 0.0092 (b1–b3) and 0.0131 (c1-c3), respectively. The micrographs confirm that cluster formation in CuO nanofluids with elapsed time after sonication where the cluster size increases with time.

The present study confirms that aggregation has a prominent role on thermal conductivity enhancement of nanofluids. However, the large aggregates and clumps formed by sedimentation have a negative impact on $k$ enhancements in nanofluids.
Fig. 4.19: The phase contrast microscopy images taken immediately after sonication, after 30 and 60 minutes of sonication for ethylene glycol based CuO nanofluids $\phi=0.0054$ (a1–a3), $\phi=0.0092$ (b1–b3), $\phi=0.0131$ (c1–c3).

### 4.4 Conclusions

Stable nanofluids exhibit moderate $k$ enhancement within the predictions of EMT. However, aggregating nanofluids show enhancement in $k$ beyond EMT predictions, immediately after sonication.

The aggregating nanofluids show a time dependent variations in $k$ with elapsed time after sonication. The highest value of $k/k_f$ is observed immediately after sonication, which decreases with elapsed time and finally reaches an equilibrium value after a time interval of about 45 min.
In the absence of stabilizers, the aggregation and the subsequent settling of agglomerates leads to a decrease in $k$ with elapsed time in aggregating nanofluids. The cluster size increases with elapsed time after sonication in aggregating nanofluids. The $\eta$ ratio also increases with time in these nanofluids. The nanofluid with low particle loading shows a least enhancement in $\eta$ with time and the extent of $\eta$ enhancement is higher for nanofluids with higher particle loading, owing to the great degree of aggregation. Moreover, a shear thinning behavior is observed for aggregating nanofluids. The optical micrographs confirm the cluster formation in unstable nanofluids with elapsed time where the cluster size increases with time.

Stable nanofluids with proper steric and electrostatic stabilization show time independent $k$ behavior with time. They show an invariant average particle size distribution and $\eta$ values with elapsed time. Sterically stabilized Ag nanofluids show no shift in plasmon resonance absorption with time and increasing metal nanoparticle concentration, indicating the absence of aggregation. The surface modified nanofluids show no aggregation (with cluster size $> 200$ nm) with time in microscopy studies.

The present results enlighten the need of surface functionalization of nanoparticles to improve the dispersion stability of nanofluids with least viscosity enhancement in order to make them ideal for practical applications.