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Experimental evidence for the significant role of initial cluster size and liquid confinement on thermo-physical properties of magnetic nanofluids under applied magnetic field

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ABSTRACT

Though huge thermal conductivity enhancement was observed in some magnetic fluids under an external field, the percentage of enhancement reported were largely different in similar magnetic fluids, which was quite perplexing to the scientific community. Here, we probe the role of initial cluster size and the liquid layer confinement between nanoparticles within chains that are formed under an external magnetic field, on thermal, rheological and interfacial property enhancement in model nanofluids. Three different ferrofluids containing oleic acid capped superparamagnetic magnetic nanoparticles (Fe_3O_4) of average crystallite sizes 9.6, 8.3 and 10.5 nm (referred as S1, S2 and S3, respectively), with different polydispersity and coating thickness, synthesized by coprecipitation technique, are used in the present study. The synthesized nanoparticles were characterized by X-ray diffraction, small angle X-ray scattering (SAXS), dynamic light scattering (DLS), vibrating sample magnetometry and thermogravimetry.

Thermal conductivity enhancement in samples S1 and S2 in the presence of magnetic field when the direction of field is parallel to the direction of heat flux were 127% (at 160 G) and 42% (at 70 G), respectively while S3 did not show significant enhancement with field. Our results suggest that in a relatively monodisperse system, nucleation occur at longer time scales and at high field strengths. On the contrary, in significantly polydisperse system, the larger particles act as nucleation centers and hence the aggregation kinetics is much faster. Under a low magnetic field strength, the particles present in S1 interact with each other and form short nanosized chains, where the growth via tip to tip aggregation is hindered by smaller particles. However in S3, larger sized particles act as nucleation centers to initiate chain formation at low field and form thick columnar structures via zippering at higher fields that lower the heat transport efficiency. Owing to the functional group, solvent molecules are trapped between the nanoparticles and the confinement of liquid molecules reduces phonon scattering at the interface. <10% enhancement in k/k_f obtained when the heat flux is perpendicular to the applied field in all three systems confirms the series mode of conduction paths. For field strength of 200 G, S3 showed 800% enhancement in viscosity while S1 and S2 showed negligible viscosity enhancement. S3 showed a significantly higher yield stress than S2 indicating that the field induced structures are stronger in S3.

The much larger thermal conductivity enhancement in samples with very small fraction of larger clusters (with minimum polydispersity) confirm the numerical simulation results that when liquids are confined in nanochannels, long range phonons are sustained by the base fluid that enhance heat transport by lowering the Kapitza resistance. These results provide several new insights into the mechanism of heat conduction in magnetic nanofluids and ways to achieve efficient heat transfer without increasing pumping power.

1. Introduction

Nanofluids have been a topic of interest during the last two decades because of anticipated benefits in heat transfer [1–4]. Of late, it is realized that the thermal conductivity enhancement in traditional nanofluids are not appropriate for heat transfer applications owing to the modest enhancement and associated issues including cost parameters [5–7]. Recent research efforts are on developing new nanofluids with large thermal conductivity enhancement. Nanofluids containing nanomaterials of larger aspect ratio and morphologies (e.g. Nanorods, CNT, Graphene) [8,9], magnetic nanofluids [10–13] and composite systems [14–19] are found to possess extraordinary thermal conductivities. Among these, magnetic nanofluids (commonly called ferrofluids) offer unique tunable thermal properties [10,20] and are found to be very promising candidates for applications in miniature electronics cooling,

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including super computers [21–25]. They are suspensions of functionalized magnetic nanoparticles in a suitable base fluid. Since the average size of the particles in a ferrofluid is around 3–15 nm, the nanoparticles are superparamagnetic in nature and in the absence of external magnetic field, the magnetic moments of the particles are randomly oriented, making the net magnetic moment of the system zero [26]. When the ferrofluid is exposed to an external magnetic field, the magnetic moments of the nanoparticles align along the field direction and the resulting dipolar interactions between the nanoparticles cause them to align as chains and columns [27]. This field induced aggregation, which can be controlled by varying the strength of the applied field and is completely reversible on removal of field, is the reason for the interesting rheological [28–31], thermal [32–34] and optical properties [35]. Hence, ferrofluids have been used in various technological applications like coolants for electronic devices [33], optical filters [36], defect sensors [37], heavy metal ion removal [38] etc.

As most of the interesting behavior of a ferrofluid in the presence of magnetic field is due to formation of field induced aggregates, for effective use of these fluids for different applications, a clear understanding of the aggregation kinetics and the factors affecting it is important. For example, the field induced increase in viscosity of ferrofluids depends on the size distribution of the nanoparticles as studies have found that the field induced aggregates are primarily made up of larger particles present in the system and most of the smaller particles remain unaggregated [39]. Recently, it was reported that aggregation kinetics of ferrofluids plays a crucial role in thermal transport as well [40]. Formation of thicker aggregates through lateral coalescence of aggregates, called zippering, reduces the number density of chains drastically, which in turn reduces the heat transport efficiency. Recently Lenin et al. [41] observed that in magnetite nanofluids with saturated fatty acids as surfactant, clustering of the nanoparticles occurred and these fluids displayed lower thermal conductivity enhancement in the presence of magnetic field, which points to the fact that adsorbed surface moieties influences the thermal properties of nanofluids. There are also some systematic studies on effect of the magnetic field direction on forced convection heat transfer enhancements in ferrofluid where the results show that the heat transfer is better enhanced when the magnetic field is perpendicular to the heat flux [24].

Thermal conductivity of nanofluids, in general, is found to increase with increase in volume fraction of the dispersed phase [42]. However, increasing the nanoparticle loading leads to an unwanted increase in viscosity and higher probability of aggregation of particles into micron sized lumps, leading to gravitational settling. Another factor that affects thermal conductivity is the aspect ratio of the nanoparticles that make up the nanofluid; the higher the aspect ratio, better the thermal conductivity [42]. However using rod shaped inclusions poses a challenge to align the rods along the direction parallel to the direction of heat flux. Also, owing to the bulkiness of the particles, nanofluids containing rod-shaped inclusions may not be stable for long periods of time. In the case of a ferrofluid on the other hand, when the field is on, the nanochain aggregates do not settle due to magnetic levitation [43]. On removal of magnetic field, the nanoparticles will be in Brownian motion rendering the ferrofluid system stable over many years. Hence, if properly formulated, ferrofluid is an excellent choice for a coolant, especially for electronic devices (MEMS, NEMS etc.) since it displays excellent heat transport capabilities that can be controlled by the application of weak fields without increase in viscosity. To make the best use of ferrofluids in various applications, a thorough understanding of the factors affecting aggregation kinetics and its role in thermo-physical properties is a prerequisite.

The objective of the current study is to understand the different factors affecting aggregation, like initial cluster size, size distribution of the nanoparticles, amount of surfactant on the nanoparticle surface and uniformity of the surfactant coating around the nanoparticles and how these factors in turn affect the thermal and rheological properties of ferrofluids in the presence of a magnetic field. With this purpose in mind, three ferrofluid systems, which differ from each other in their particle size distribution and surface chemistry were synthesized in our laboratory and the prepared particles were characterized by X-ray diffraction studies to obtain the average crystallite size, small angle X-ray scattering (SAXS) for the distance distribution curve, dynamic light scattering (DLS) technique for the average hydrodynamic size and polydispersity index, vibrating sample magnetometry for saturation magnetization and thermogravimetry for obtaining the amount of surfactant present on the nanoparticle surface. The field tunable thermal transport in all three systems was probed for the role of the surfactant in lowering interfacial thermal boundary resistance and the effect of confinement of liquid molecules by the field induced aggregates. The effect of polydispersity, particularly the role of larger aggregates in a ferrofluid system, on the structural strength of the field induced aggregates which controls the rheological characteristics of a system are also studied.

2. Materials and methods

Three different ferrofluid systems with oleic acid capped magnetic nanoparticles (Fe_3O_4) of same volume fraction ($\Phi = 0.037$), dispersed in kerosene as the carrier fluid were synthesized by coprecipitation technique [44,45]. The average crystallite sizes of the particles were 9.6, 8.3 and 10.5 nm, respectively. These samples are referred to as S1, S2 and S3, respectively. Magnetite nanoparticles in the size range 7–10 nm are chosen for this owing to their long term stability and superparamagnetic behavior. Rigaku Ultima IV was used to carry out X-ray diffraction measurements to obtain the average crystallite size, with 2θ values ranging from 20–80° at a scan rate of 2°/min and the wavelength of Cu Kα radiation was 1.5416 Å. Small angle X-ray scattering measurements were also carried out using the same system, Rigaku Ultima IV, where the samples in dilute form were placed inside a rotating capillary attachment that was rotated at 50 rpm. The measurements were performed in the angle range, 0.01 to 2.2°. Hydrodynamic size of the oleic acid capped nanoparticles of all three systems was obtained through dynamic light scattering (DLS) studies using Malvern's Zeta Nanosizer (ZEN 3600). Here the Brownian motion of the particles is exploited to obtain an intensity correlation function which gives the diffusion coefficient from which the hydrodynamic size is calculated using the Stokes-Einstein equation. DLS measurements were performed on diluted samples and the wavelength of laser light was 632 nm. The magnetization curve of the surfactant capped nanoparticles, in the field range $\pm$ 1.5 T at room temperature, was obtained using cryogen free vibrating sample magnetometer (Cryogenics Ltd., UK). Mettler Toledo 1100F was used to perform thermogravimetric measurements in the temperature range of 30–650 °C at a heating rate of 10 °C/min in oxygen atmosphere. LEICA DM IRM inverted phase contrast microscope equipped with ORCA-Flash 4.0 LT camera of Hamamatsu was used for optical imaging. Transient hot wire method was used for thermal conductivity measurements. In all thermal conductivity measurements, a custom made solenoid was used as the source of magnetic field. The strength of the magnetic field was measured using a F. W. Bell Gauss meter (model number: 5080). In the region where sample was placed, the field is fairly uniform with $\pm$3 G. For the field dependent study, measurements were taken after 30 s of setting the field to required magnitude. To study the variation of thermal conductivity with time, after the field strength was set to a constant magnitude, each measurement, of duration 1.5 min., was taken after a time gap of 1 min. Anton Paar MCR 301 was used for rheological characterization of the samples with parallel plate geometry at a gap height of 0.1 mm. In this case the source of magnetic field is an in-built Helmholtz coil where the variation in magnetic field is <1 G. For viscosity measurements under magnetic field sweep, the shear rate was fixed at 75/s and for the amplitude sweep the frequency was fixed at 10 rad/s. All the samples were presheared for 1 min at constant shear rate of 100/s. For the amplitude sweep, the preshear was followed by standing time of another 1 min