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Research articles

Role of field-induced nanostructures, zippering and size polydispersity on effective thermal transport in magnetic fluids without significant viscosity enhancement

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ABSTRACT

Magnetic nanofluids or ferrofluids exhibit extraordinary field dependant tunable thermal conductivity (k), which make them potential candidates for microelectronic cooling applications. However, the associated viscosity enhancement under an external stimulus is undesirable for practical applications. Further, the exact mechanism of heat transport and the role of field induced nanostructures on thermal transport is not clearly understood. In this paper, through systematic thermal, rheological and microscopic studies in 'model ferrofluids', we demonstrate for the first time, the conditions to achieve very high thermal conductivity to viscosity ratio. Highly stable ferrofluids with similar crystallite size, base fluid, capping agent and magnetic properties, but with slightly different size distributions, are synthesized and characterized by X-ray diffraction, small angle X-ray scattering, transmission electron microscopy, dynamic light scattering, vibrating sample magnetometer, Fourier transform infrared spectroscopy and thermo-gravimetry. The average hydrodynamic diameters of the particles were 11.7 and 10.1 nm and the polydispersity indices (σ), were 0.226 and 0.151, respectively. We observe that the system with smaller polydispersity ($\sigma = 0.151$) gives larger k enhancement (130% for 150 G) as compared to the one with $\sigma = 0.226$ (73% for 80 G). Further, our results show that dispersions without larger aggregates and with high density interfacial capping (with surfactant) can provide very high enhancement in thermal conductivity, with insignificant viscosity enhancement, due to minimal interfacial losses. We also provide experimental evidence for the effective heat conduction (parallel mode) through a large number of space filling linear aggregates with high aspect ratio. Microscopic studies reveal that the larger particles act as nucleating sites and facilitate lateral aggregation (zippering) of linear chains that considerably reduces the number density of space filling linear aggregates. Our findings are very useful for optimizing the heat transfer properties of magnetic fluids (and also in composite systems consisting of CNT, graphene etc.) for the development of next generation microelectronic cooling technologies, thermal energy harvesting and magnetic fluid based therapeutics.

1. Introduction

Ever since the early reports of anomalous thermal conductivity enhancement in nanoparticle dispersions, popularly known as nanofluids, there has been tremendous interest in this field because of potential heat transfer applications [1,2]. Subsequent benchmark study led by Buongiorno et al. [3] and many other studies, conclusively proved that stable nanofluids provide only modest thermal conductivity enhancement within Maxwell's predictions, which necessitated the need to develop new nanofluids with high thermal conductivity at low particle loading to prevent the undesired effects of rheological property enhancements. Suspensions of carbon nanotubes [4], ferrimagnetic particles or ferrofluids [4–6], graphene oxide nanofluids [7] etc. have been shown to exhibit anomalous thermal conductivity enhancements under certain conditions. Among these, ferrofluids, suspensions of fine magnetic nanoparticles, are found to be a promising material [8]. Since the early report of tunable thermal conductivity in ferrofluids by Philip et al. [5], the interest in this material have drastically increased because of the potential applications in microelectronics cooling and also from a fundamental perspective [9]. Several subsequent studies have also reported very high k enhancement in ferrofluids under an applied magnetic field. Thermal transport in ferrofluids have been extensively studied experimentally both under stationary [5,10–12] as well as flow conditions [13–16]. Increasing the

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volume fraction of nanoparticles in the base fluid and increasing the temperature were found to increase the thermal conductivity of nanofluids [17–24]. Thermal conductivity of ferrofluids is highly anisotropic since maximum enhancement in thermal transport is observed when the applied field is parallel to the direction of heat flux [25–27]. Altan et al. [28] found that for magnetite nanoparticles in water and heptane, enhancement in heat transport is possible only when temperature gradients are present due to thermomagnetic convection. Alternating magnetic field is found to enhance forced convection heat transfer [29]. Ferrofluids containing hybrid magnetic nanoparticles were synthesized to improve thermal conductivity. Sun et al. [30] prepared magnetic graphite nanoflake suspension and they obtained a maximum thermal conductivity enhancement of 325% with a particle loading of just 0.8% w/w. Graphene-magnetite hybrid nanofluids improved heat transport by 82% under forced laminar flow [31]. To understand the role of base fluid viscosity on thermal conductivity of ferrofluids, Tsai et al. [32] varied the viscosity of ferrofluid containing magnetite nanoparticles in diesel oil and polydimethyl siloxane by changing the volumetric fractions of the two liquids that make up the base fluid. Some additives like gum arabic coated carbon nanotubes [20] and diamond microparticles [33] were found to increase thermal conductivity of ferrofluids. Hong et al. [34] used carbon nanotubes as an additive in Fe_2O_3 based aqueous ferrofluid and they reported enhanced thermal conductivity in the presence of field since the field induced aggregates aligned the carbon nanotubes along the field direction resulting in better contact amongst themselves which in turn improves heat transport. Karimi et al. [35] compared thermal conductivity of water-based ferrofluids containing two different magnetic nanoparticles, Fe_3O_4 and $CoFe_2O_3$. Lenin et al. [36] investigated the role of primary and secondary surfactant layers in heat transport in lauric acid coated magnetite ferrofluids.

Though tunable thermal conductivity in ferrofluids is conclusively proven by various groups, the exact mechanism of heat transport, the reasons for the different percentage of k enhancement reported in samples with similar volume fractions and the ideal conditions to achieve large k enhancement with minimum magnetic field strength are still unclear. Such an understanding is a prerequisite to optimize the thermal conductivity enhancement in ferrofluids, which is extremely important to reduce the cost factor and also the sample volume.

The questions we try to address from this study are the following: (a) What is the role of nano/microstructures, formed under the magnetic stimulus, on thermal and rheological properties? (b) What is role of polydispersity or contributions of larger particles or aggregates on thermal conductivity and rheological enhancement under a magnetic field? (c) What is the role of capping agent on interfacial thermal conductance and heat transport? (d) What is the cause for lowering of k enhancement beyond a critical magnetic field? To answer these questions, the thermal and rheological properties of two ferrofluids of similar crystallite size, capping agent and magnetic properties, but with slightly different size distributions, are synthesized in our laboratory [10]. The prepared particles are characterized by X-ray diffraction, small angle X-ray scattering, transmission electron microscopy, dynamic light scattering, vibrating sample magnetometer, Fourier transform infrared spectroscopy and thermogravimetry, for obtaining crystallite size, particle morphology, particle size distribution, hydrodynamic size distribution, magnetic properties, nature of capping on nanoparticles and amount of surfactant present, respectively. To understand the nano to microstructural evolution under magnetic field, phase contrast optical microscopic studies (both field and time dependent) was carried out under different experimental conditions. Finally, the effect of liquid layering and the change in interfacial thermal boundary resistance due to the surfactant coating are analyzed and compared with existing theories and experimental findings.

2. Materials and methods

Oleic acid capped iron oxide (Fe_3O_4) nanoparticles were synthesized using chemical coprecipitation technique [37,38]. The two different ferrofluids employed in this study, named F1 and F2, were oil based (kerosene) and the volume fraction of the dispersed phase was 0.037. F1 and F2 showed excellent stability over several years. The XRD measurements were performed using Rigaku Ultima IV with 2θ values ranging from 20 to 80° at a scan rate of 2°/min. The wavelength of the Cu Kα radiation used was 1.5416 A°. Rigaku Ultima IV was used for SAXS measurements in the angle range, 0.01 to 2.2° with the samples inserted in a rotating capillary attachment, which is rotated at a speed of 50 rpm. Cryogen free vibrating sample magnetometer (Cryogenics Ltd., UK) was employed to obtain the magnetization curve of the superparamagnetic iron oxide nanoparticles in the field range of ±1.5 T at room temperature. JEOL JEM 2100 high-resolution transmission electron microscope was used to obtain the size distribution of the nanoparticles. AB BOMEM MB 3000 FTIR spectrometer, in the spectral range, 500–3500 cm^{-1}, was used to confirm surface functionalisation of the nanoparticles. Thermogravimetric measurements on powder samples were performed using Mettler Toledo 1100F where the temperature was varied from 30 to 650 °C at a heating rate of 10 °C per minute in oxygen atmosphere. Dynamic light scattering measurements to obtain the size distribution were carried out using Malvern's Zeta Nanosizer (ZEN3600) which utilizes Brownian motion of the particles to obtain the intensity correlation from which the hydrodynamic size is obtained using Stokes-Einstein equation, $R_H = k_B T/6\pi\eta D$, where R_H is the hydrodynamic size, T is the temperature, η is the viscosity of the base fluid and D is the diffusion coefficient. Optical images were obtained using LEICA DM IRM inverted phase contrast microscope with ORCA-Flash 4.0 LT camera of Hamamatsu at a magnification of 40×/100×. Thermal conductivity measurements were performed using transient hot wire method [5].

To ensure the accuracy of the thermal conductivity values, measurements were carried out using three standard liquids: water, ethylene glycol and kerosene, where the measured values are in good agreement with the literature results. The measurements in these three samples are independently performed using a Hot Disk Thermal Constants Analyser TPS 2500s and the results were comparable. For all thermal conductivity measurements including measurements with different field orientations, the magnetic field of required strength was obtained by varying the current through a solenoid. Except for time studies, every measurement was made after a time gap of 30 s after setting the field to a desired magnitude at 25 °C. Rheological characterization of the samples was done using Anton Paar MCR 301 rheometer with an in-built Helmholtz coil setup to produce a uniform magnetic field. In this study, all the tests were done using parallel plate geometry with a gap height of 0.1 mm at a constant temperature of 25 °C.

3. Results and discussions

3.1. Crystallite size and distance distribution

The XRD diffraction pattern of F1 and F2 are shown in Fig. 1(a). Both the samples showed diffraction peaks due to scattering from (220), (311), (400), (422), (511) and (440) planes which corresponds to an inverse spinel structure (JCPDS card No. 89-3854). The crystallite sizes of the particles were estimated from the full width at half maximum of the maximum intensity peak, (311),