Nano Today (2012) 7, 124–136

Available online at www.sciencedirect.com

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journal homepage: www.elsevier.com/locate/nanotoday

REVIEW

Heat conduction mechanisms in nanofluids and suspensions

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Received 1 December 2011; received in revised form 13 February 2012; accepted 20 February 2012

KEYWORDS
Nanofluids;
Graphite suspensions;
Clustering;
AC impedance spectroscopy;
Thermal conductivity;
Phase transition

Summary Nanofluids, liquids containing suspensions of nanoparticles, have been reported by some groups to exhibit substantially higher thermal conductivity than that of their corresponding base fluids that cannot be explained by existing theories. However, the reported high thermal conductivity sometimes cannot be reproduced by others. Potential mechanisms leading to this enhancement are still under scrutiny. In this paper, we first take a critical review of heat conduction mechanisms proposed in literature, and then summarize our work. Our experimental studies demonstrate that nanoparticle clustering is the key contributor to the thermal conductivity enhancement. Guided by this insight, we use graphite flakes as additives and develop a method to prepare stable graphite suspensions with large thermal conductivity enhancement in water and oil. We also observe thermal percolation phenomenon and explained the phenomenon based on combined optical and AC impedance spectroscopy studies. We demonstrate temperature regulation of electrical and thermal properties of graphite suspensions through solid—liquid phase change, which may potentially be useful in energy systems in the future.

Introduction

Nanofluids — colloids obtained by mixing nanoparticles with a base fluid — have attracted wide attention since Choi coined the term in 1995 and observed that they have much higher thermal conductivity than anticipated from the effective medium theories [1—7]. In fact, adding particles into a liquid to improve its thermal conductivity is an old idea. Researchers have tried to add micron sized or larger solid particles into liquids to increase their thermal conductivity, as solids usually have much higher thermal conductivity than liquids [8]. The thermal conductivity of these suspensions can be predicted by the effective medium theory, which was originated from Maxwell [9] and continuously improved by many researchers to include factors such as interfacial thermal resistance between the particles and the base fluid, and shape of the particulates [10—13]. However, large particles are prone to settling out of the suspensions. There are also some other drawbacks that limit the applications of

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doi:10.1016/j.nantod.2012.02.007

fluids loaded with large particles [8,14,15], as the particles are likely to: (1) clog the flow channel, (2) abrade the surface of fluid channel, and (3) increase the pressure drop. As an alternative, researchers drew the attention from using large particles to dispersing nanoparticles into the liquids. In fact, Masuda et al. [16] investigated the thermal conductivity and viscosity of suspensions containing alumina, silica, and titanium dioxide nanoparticles before Choi et al.'s studies [1]. Current interest towards nanofluids is fueled by both fundamental science and applications. On the fundamental side, mechanisms of heat conduction and enhanced thermal conductivity in nanofluids are of great interest [17—20]. On the application side, the enhanced thermal conductivity of nanofluids promises applications in thermal systems [21—23].

Since its interception, nanofluids have been a controversial topic. First, some previously reported high thermal conductivity cannot be repeated by others [24—27]. This has raised questions on the accuracy of the experimental method. However, a world-wide round-robin involving 33 laboratories has shown reasonable consistency in thermal conductivity measurement methods, especially the widely used transient hot-wire method, despite the fact that nanofluids studied by the round-robin groups did not show anomalous increase in thermal conductivity [28]. Second, many potential mechanisms have been proposed on why thermal conductivity can be increased beyond the effective medium theories, although careful reasoning can rule out most of them [18,29,30]. Fueled by these controversies, publications on nanofluids continue to increase, and many reviews are written.

The purposes of this article are to summarize our understanding of heat conduction mechanisms in nanofluids, arising from our past work in this area [19,31—39] and our knowledge of other studies in this field. Due to the large number of existing reviews [3—7,40—43], we do not intend to give a systematic summary of past work in the literature. We will first discuss potential mechanisms that can affect heat conduction in nanofluids. Most of these mechanisms have already been discussed in literatures, but we bring in additional insights from our understanding of heat conduction in solids and liquids, and Brownian motion. Like several previous theoretical analysis [44—48], we believe clustering is the key mechanism for thermal conductivity enhancement. Our conclusion is mostly based on our own experimental observations. This understanding led us to develop graphite-flake based suspensions. The graphite flakes have several tens of nanometers in thickness, but several microns in lateral size. These suspensions fall in between nanofluids and microfluids, and can be made stable in oil as well as in water. Although there have already been reports that such suspensions can have much enhanced thermal conductivity [49—51], we will show new experimental observations, such as thermal percolation, and demonstrate reversible regulation of electrical and thermal conductivity of such suspensions going through liquid—solid phase change process in addition to achieving very high thermal conductivity values. We will conclude this paper by proposing a few interesting research directions arising from past work.

Heat conduction mechanisms in nanofluids

We will first summarize heat conduction mechanisms in solid, liquid, and solid—liquid interface, then move on to elaborate on potential mechanisms that can affect heat conduction in nanofluids.

Heat conduction mechanisms in solids, liquids, and liquid—solid interfaces

Heat conduction in solids

Most heat in crystalline dielectric and semiconductors is carried by phonons, which are quantized lattice vibrations [52]. At or above room temperature, the thermal conductivity of bulk crystalline solids usually decreases with increasing temperature. Phonons in crystalline solids have a wide range of mean free paths. According to kinetic theory, the thermal conductivity can be expressed as

$$k = \frac{1}{3}\int C(\omega)\,v(\omega)\,\Lambda(\omega)\,d\omega = \frac{1}{3}Cv\Lambda \tag{1}$$

where C is the specific heat per unit volume, v the phonon group velocity, and Λ the mean free path. The first equality emphasizes that these quantities all depend on the frequency of the phonon vibration in the solid, while the second equality is often used to estimate the phonon mean free path based on measured thermal conductivity values, specific heat and the speed of sound. Due to the neglect of the frequency dependence, the latter equality can cause large errors. In Si, for example, phonons with a mean free path less than 10 nm, 100 nm, and 1 μm contribute about 1%, 30%, and 60%, respectively, to the total thermal conductivity of 136 W/(m K), according to first principle simulations at room temperature [53,54], while the second equality will give a phonon mean free path of only 40 nm. At or above room temperature, the thermal conductivity of bulk crystalline solids usually decreases with increasing temperature, because at high temperatures, the mean free path decreases with increasing temperatures due to phonon—phonon scatterings. In amorphous solids, the phonon picture is less valid due to lack of periodicity in the arrangement of atoms. Thermal conductivity near room temperature in amorphous solids roughly follows the trend of specific heat (i.e., slowly increases with temperature to saturation), due to the short lifetime of vibrational modes. Roughly, the phonon mean free path in Eq. (1) is the same order as atomic separations. In metals, electrons dominate the heat conduction, and Eq. (1) applies if each quantity represents that of electrons. The mean free paths of electrons in metals are usually very short, on the order of a few nanometers [55]. The thermal conductivity of metals typically decreases with increasing temperature due to increased scattering of electrons at higher temperatures.

The thermal conductivity of individual nanoparticles is difficult to measure. However, it is anticipated that as the diameter of nanoparticles becomes comparable to the phonon's or electron's mean free path in bulk materials, the distance that these carriers can travel are limited to roughly the diameter of the nanoparticle. Hence, the temperature dependence of thermal conductivity of very small nanoparticles should be similar to that of their specific heat, i.e.,