Thermal Percolation in Stable Graphite Suspensions

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ABSTRACT: Different from the electrical conductivity of conductive composites, the thermal conductivity usually does not have distinctive percolation characteristics. Here we report that graphite suspensions show distinct behavior in the thermal conductivity at the electrical percolation threshold, including a sharp kink at the percolation threshold, below which thermal conductivity increases rapidly while above which the rate of increase is smaller, contrary to the electrical percolation behavior. Based on microstructural and alternating current impedance spectroscopy studies, we interpret this behavior as a result of the change of interaction forces between graphite flakes when isolated clusters of graphite flakes form percolated structures. Our results shed light on the thermal conductivity enhancement mechanisms in nanofluids and have potential applications in energy systems.

KEYWORDS: Thermal, percolation, graphite, suspension
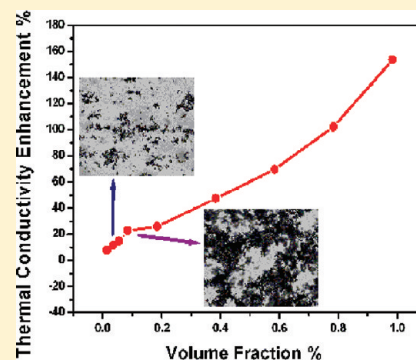
Although percolation of electrical conduction in composites and suspensions has been observed and well understood,[1,2] no distinctive percolation features in thermal conductivity have been reported.[3−5] For example, carbon-based materials (carbon nanotubes and fibers, graphite flakes, and graphenes) have been widely utilized as additives to form composite material[1,6] and suspensions,[7−9] because of their high in-plane strength and electrical and thermal conductivity. Sharp increase in the electrical conductivity of carbon-based composites and suspensions above the percolation threshold has been well-documented and studied.[10,11] However, no distinctive features in the thermal conductivity at the percolation threshold have been observed.[12] The addition of carbon-based materials and other types of nanoparticles into a liquid has led to, in some cases, anomalous increase,[7,13] while in other cases, no obvious enhancement in the thermal conductivity.[14] Mechanisms for such thermal conductivity enhancements have been debated extensively.[15−18] It is generally believed that the percolation does not lead to sharp transitions in the thermal conductivity, due to persistent heat conduction in the matrix phase and the relatively smaller contrast in the thermal conductivity of the fluids and the percolating phase.[3−5]

We will show in this paper that thermal conductivity values of graphite suspensions depend sensitively on the internal structure and report the experimental observation of distinct percolation behavior in the thermal conductivity at the electrical percolation threshold, including a sharp kink at the percolation threshold, below which thermal conductivity increases rapidly while above which the rate of increase is smaller, contrary to the electrical percolation behavior. Microstructural and alternating current (AC) impedance spectroscopy studies suggest that this kink arises from the change in the bonding strength between graphite flakes as the suspensions going through a transition from isolated clusters to percolated structures. Our study sheds light on the understanding of heat conduction in composites and nanofluids. Our experimental observation of the bonding change among graphite flakes during the structural transition from isolated clusters to percolated clusters sheds new insights on colloidal states and gelation processes.[19,20] The achieved high thermal

conductivity values with small graphite loading have potential applications in energy systems.

We followed a process of sulfuric acid intercalation, microwave expansion, and ultrasonic dispersion to make graphite suspensions.[21−23] After these processes, natural graphite is exfoliated into graphite flakes, which are then mixed with ethylene glycol (EG) and poly α-olefin oil (PAO) to form a stable suspension without additional surfactants. The graphite flakes have the diameter of several micrometers and the thickness of several tens of nm (Figure 1a,b). The high-
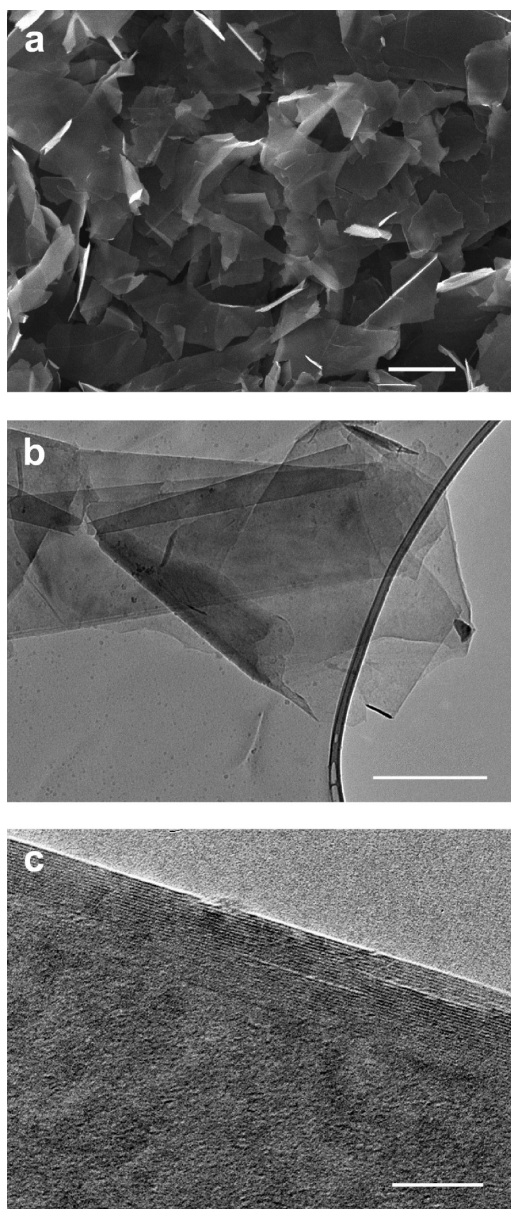
thermal conductivity of the graphite suspensions, different methods, direct sonicating at different volume fraction and diluting from high volume fraction, are employed to prepare samples with different graphite volume fractions.

Thermal conductivity of graphite suspensions was measured using the transient hot wire method developed by Nagasaka and Nagashima.[24] Such graphite suspensions have excellent heat transfer property. The thermal conductivities of 1% (V/V) graphite/PAO, graphite/EG suspensions at room temperature reach 0.436 and 0.634W/mK (Figure 2A). Comparing to that
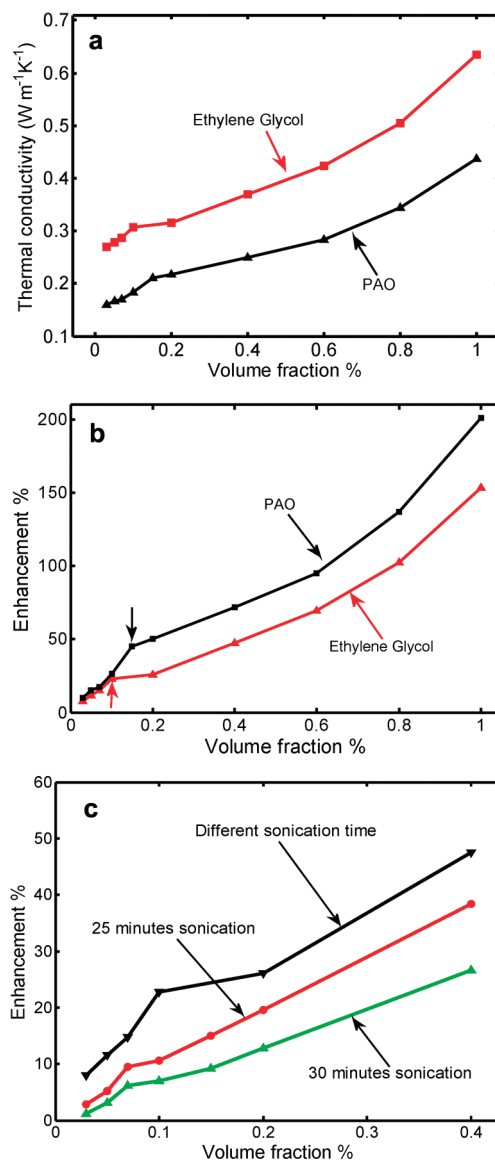

Figure 1. Micrographs of graphite flakes. (a) SEM image of graphite flakes obtained by the H_2SO_4 intercalation, microwave expansion, and ultrasonic exfoliation of natural graphite; scale bar: 2 μm. (b) Typical TEM imagine of a graphite flake; scale bar: 500 nm. (c) HRTEM image of a graphite flake; scale bar: 10 nm.

Figure 2. (a) Measured thermal conductivity of two types of graphite suspensions as a functional of the graphite volume fraction, both showing a kink behavior; (b) relative enhancement in thermal conductivity; and (c) thermal conductivity of EG/graphite suspensions prepared at different conditions. Two series of samples were diluted from concentrated suspensions ultrasonicated for 25 and 30 min. One set of samples (shown in black) was prepared by dispersing graphite flakes in EG by ultrasonication for different times, from (3−15 min), depending on the volume fraction of graphite flakes.

resolution transmission electron microscopy (HRTEM) image indicates that these flakes are composed of several layers of hexagonal lattice (Figure 1c), and the distance between planes is 0.335 nm, which is consistent with the distance of layers of natural graphite. In order to elucidate the kink behavior in the

of pure PAO (0.145W/mK), EG (0.25 W/mK), thermal conductivity enhancements, defined as $(k_e - k_f)/k_f$ in which k_e and k_f are the thermal conductivity of the suspension and the
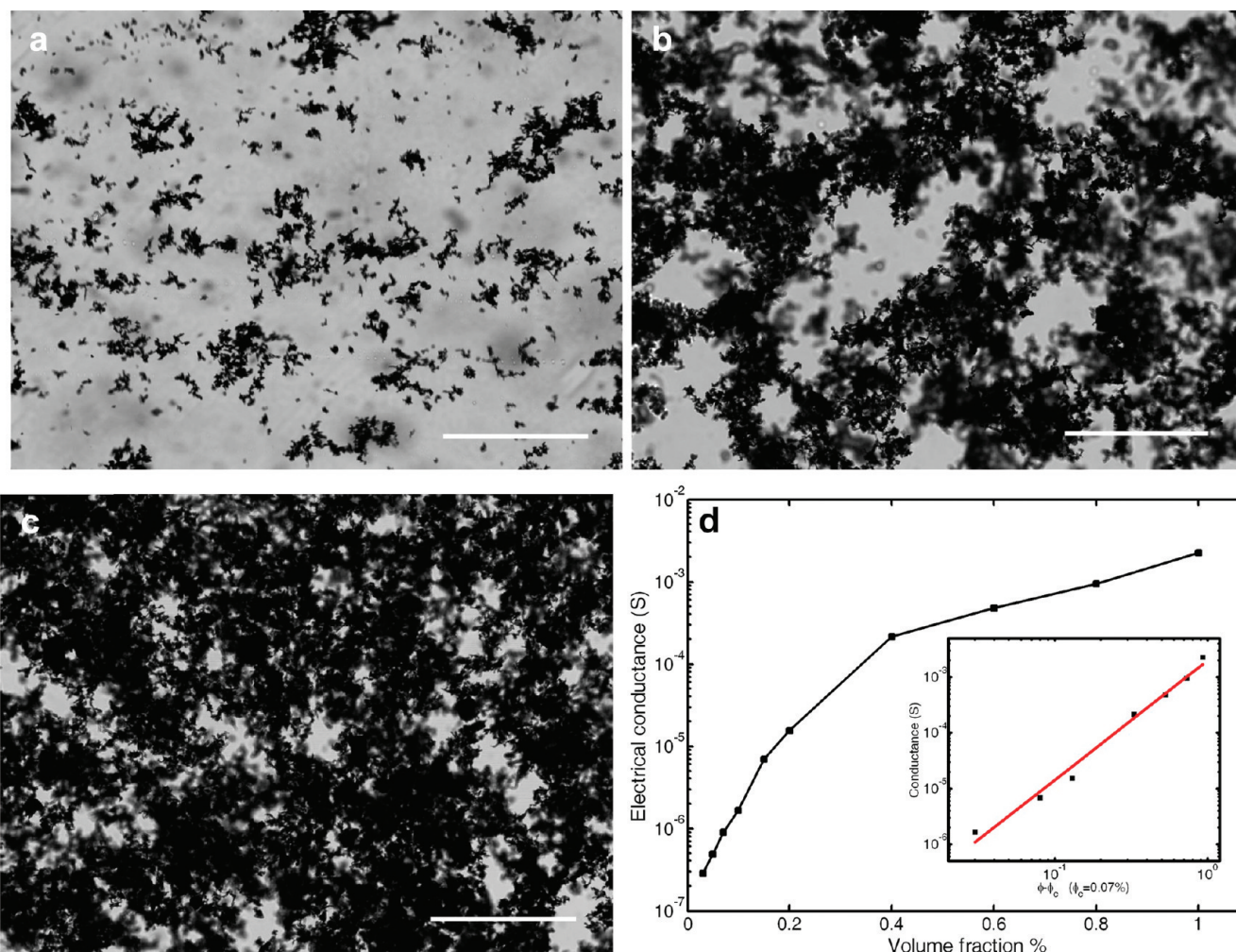
Figure 3. Optical micrographs of the microstructures of graphite/EG suspensions at three volume fractions: 0.03% (a), 0.1% (b), and 0.2% (c). Scale bars in a–c are all corresponding to 200 μm. (d) Electrical conductance shows a percolation behavior at 0.07%.

base fluids, respectively, reach 201% (graphite/PAO) and 153% (graphite/EG), as shown in Figure 2b. Thermal conductivity values of such solutions depend quite sensitively on the preparation conditions. Sonication time has a strong influence on thermal conductivity as shown in Figure 2c. In this figure, graphite solutions were prepared under three different conditions. For the 25 and 30 min curves, a high volume-fraction graphite suspension was first prepared at the specified sonication time, and lower volume-fraction suspensions were derived by diluting the original suspensions. The samples prepared with shorter sonication times for different volume fractions have the highest thermal conductivity. SEM analysis has shown that longer sonication times reduces in-plane dimension of graphite flakes.

The graphite suspension not only has high thermal conductivity but also shows peculiar dependence on the volume fraction of the graphite flakes. There are two extraordinary features in the volume fraction dependence of thermal conductivity enhancement. First, there is a sharp kink in the thermal conductivity dependence on the volume fraction at certain volume fractions. At the kink point, the thermal conductivity value is continuous, but the slopes changed sharply. Second, below the kink point, thermal conductivity increases more rapidly with volume fraction than that of above the kink point. This behavior is completely opposite to the behavior of the

electrical conductivity, which grows rapidly after percolation. In addition, we observed that longer sonication time leads to smaller thermal conductivity and typically a lower critical volume, although the latter is not apparent in Figure 2c because the sonication time is long. The kink in thermal conductivity may be related to percolation. However, it is well-known that the percolation does not lead to sharp transitions in the thermal conductivity, due to persistent heat conduction in the matrix phase and the relatively smaller contrast in the thermal conductivity of the fluids and percolating phase.[3−5] Furthermore, it is generally anticipated that the rate of the thermal conductivity increase after the onset of percolation will be much higher, contrary to our experimental observations.

The peculiar thermal conductivity behavior is related to various states of soft materials.[19,20] At low volume fraction, graphite flakes form isolated clusters evenly distributed in EG (Figure 3a). Such clusters are stable due to long-range repulsion and short-range attraction in the suspensions.[25,26] With the increase of graphite loading, we observed an increase in the cluster size, population, and packing. At 0.1% and 0.2% volume fraction of graphite/EG suspension, these clusters connect each other and form a percolated 3D network within EG (Figure 3b,c). Electrical resistance measurements show that the solutions have a percolation threshold at 0.07%

volume fraction (Figure 3d), consistent with microstructural observations.

Impedance spectroscopy is employed to separate the bulk, grain boundary, and electrode processes of polycrystalline materials.[27] Here, we study the impact of structural transformation on the transport properties using AC impedance spectroscopy. Figure 4a shows Nyquist plots[28] of the real and
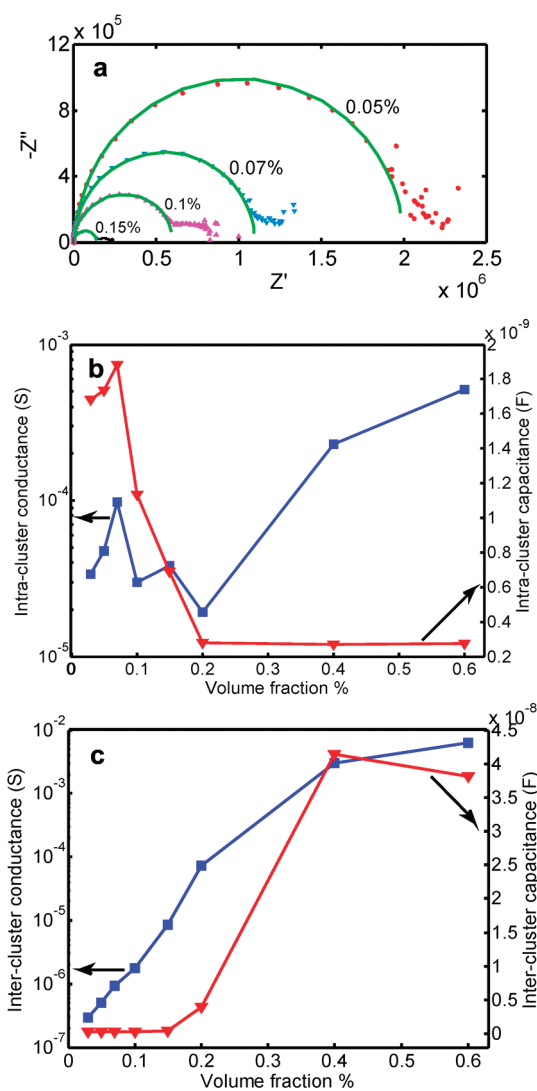

Figure 4. Electrical characteristics of EG/graphite suspensions corresponding to the red curve in Figure 2(c) (25 min ultrasonic time). (a) Nyquist plots of AC impedance of EG/graphite suspensions at different volume loadings, and (b) intra- and (c) intercluster conductance and capacitance as a function of graphite volume fraction.

imaginary plot of AC impedance for several volume fractions for samples prepared corresponding to 25 min sonication time in Figure 3c. Each impedance curve consists of two parts: a large semicircle-like part and a tail part. We associate the tail part as the electrode response and the large semicircle to the combined response of the intra- and inter- graphite clusters. We modeled the intra- and intercluster impedance responses by two RC parallel circuits in series. The characteristic frequency ω_0 of a RC parallel unit is determined by $\omega_0 = 1/RC$. The RC unit with higher characteristic frequency represents the intra-cluster impedance response, while the RC unit with lower characteristic frequency represents the intercluster impedance

response. Green curves in Figure 4a are obtained by using this model, and dots are experimental points, showing good agreements between the two. The resistance and capacitance values of the intercluster and intracluster impedances are extracted and plotted in Figures 4b,c. We note that immediately after the electrical percolation threshold (between 0.07% to 0.2% volume fraction loading, Figure 4b), both intracluster capacitance and conductance decrease with increasing graphite loading, while the intercluster conductance increases rapidly (Figure 4c).

Based on the microstructural evolution and AC impedance spectroscopy studies, the mechanism of the sharp inflection of thermal conductivity can be explained as follows: Below the percolation threshold, graphite flakes form clusters. These clusters tend to minimize the surface energy via tighter binding among the graphite flakes. As the clusters merge to form a percolation network, the driven force to minimize surface energy becomes smaller, and the binding between graphite flakes becomes weaker, and graphite flake separations increases, which leads to decreased flake-to-flake (intracluster) conductance and capacitance (Figure 4b) but an increase in the intercluster conductance (Figure 4c) between the volume fraction of 0.07−0.2%. As the flake−flake separation increases within the cluster, thermal interface resistance between graphite flakes increases, leading to slower rate of increase at high volume fractions. When the volume fraction increases (>0.2%) further, it no longer makes much sense to separate the suspension into two regimes, and hence one should not pay attention to the intracluster conductance and capacitance trends at large volume fractions.

Our experiments also provide insights into the conflicting experimental results in the nanofluids field.[7,13,14] Most previous experimental data on spherical nanoparticles have not reached the percolation phase transition point, and transport lies in either isolated particle or isolated cluster regimes. A similar kink behavior can be seen in the thermal conductivity data of CuO nanofluids,[29] although the paper did not discuss the behavior. High aspect ratio nanoparticles, such as carbon nanotube-based nanofluids, have a lower percolation threshold, and experiments in the past are already in the percolated regime. Our understanding is also instructive for achieving high thermal conductivity in dilute suspensions. First, thermal conductivity enhancement is due to heat conduction within the solid, and hence high thermal conductivity additives should be used. Second, high thermal conductivity additives that are easy to form clusters will not only help to stabilize suspensions but also to enhance the thermal conductivity at low volume fractions. Third, high interface density in the suspensions will effectively suppress the thermal conductivity enhancement because the interface thermal resistance is detrimental to thermal transport. Hence, particulates with high aspect ratio (such as carbon nanotubes and graphite flakes), by forming tightly bonded clusters and suppressing the interface resistance, can become excellent additives to achieve high thermal conductivity.

Above the percolation threshold, the suspension becomes vary viscous and gel like. Gelation is a complicated process and a topic of great interest for a wide range of applications.[30,31] The thermal conductivity behavior we observe as well as the AC impedance spectroscopy technique we applied to the understanding of the transport processes should have bearing to this general topic.

In summary, we observed peculiar behavior of the thermal conductivity of the suspensions at the percolation threshold,

including a sharp kind and a more rapid growth below, rather than above the percolation threshold, contrary to the rapid increase in the electrical conductivity above the percolation threshold. We interpret this transition as a result of the change of interaction forces between graphite flakes when isolated clusters percolate to form a 3D network and the corresponding change in the contact resistances between graphite flakes. Our experiments not only shed light on heat conduction mechanisms in nanofluids but also lead to new insights on colloidal states and gelation processes. The excellent thermal conductivity of the graphite suspensions, together with the low-cost synthesis method, suggests that these fluids may find applications in many energy systems, such as thermal convection[9] and thermal storage.[23]

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