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# The thermal conductivity of clustered nanocolloids

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We quantify the effect of clustering on the thermal conductivity of colloidal dispersions using silane-treated silica, a system engineered to exhibit reversible clustering under well-controlled conditions. We show that the thermal conductivity increases monotonically with cluster size and spans the entire range between the two limits of Maxwell's theory. The results, corroborated by numerical simulation, demonstrate that large increases of the thermal conductivity of colloidal dispersions are possible, yet fully within the predictions of classical theory. © *2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.* [http://dx.doi.org/10.1063/1.4880975]

The presence of solid particles in a fluid is known to increase the thermal transport properties of the dispersion over that of the base fluid and the generally large difference between the conductivity of the two phases leads to significant improvements even at low volume fraction of the solid.[1,2] This has suggested a remarkably simple way to improve the thermal conductivity of thermal fluids (which is generally low), through the dispersion of small amounts of a dispersed solid. The energy savings that could be achieved by colloidal thermal fluids (nanofluids) has prompted several investigations into their thermal properties, and particularly into the enhancement of the thermal conductivity of the base fluid in the presence of colloidal particles.[3–9] The precise magnitude of the enhancement has generated a debate in the literature that has centered on reports of anomalously large enhancements relative to those predicted by standard theories,[2] and on the possible mechanisms that could explain such large enhancements.[10,11] The classical theory of heat conduction in inhomogeneous media was developed by Maxwell, originally in the context of electrical conduction, and gives the thermal conductivity of a two-phase system that consists of a dispersion of non-interacting spheres in a continuous medium.[12] At fixed volume fraction of phases, Maxwell's theory predicts in fact two limits:[13,14]

$$1 + \frac{3\phi_p(k_p - k_f)}{3k_f + (1 - \phi_p)(k_p - k_f)} \le \frac{k}{k_f} \le \frac{k_p}{k_f}\left(1 - \frac{3(1 - \phi_p)(k_p - k_f)}{3k_p - \phi_p(k_p - k_f)}\right). \qquad (1)$$

Here, $k$ is the conductivity of the dispersion, $k_p$ and $k_f$ are the conductivities of the solid and liquid, respectively, and $\phi_p$ is the volume fraction of the solid phase. The lower bound corresponds to a dispersion of the phase with the higher conductivity into a continuum formed by the phase with the lower conductivity and represents the standard model for a well-dispersed colloid. The upper bound corresponds to a system in which the phases are inverted, such that the high-conductivity phase forms the continuous medium into which the low-conductivity phase is dispersed. The upper limit has been proposed as a model for colloidal clusters based on the idea that the interconnected structure of an aggregated colloid establishes continuous pathways of high thermal conductivity.[14,15] In this view, the conductivity of a colloidal dispersion at a fixed volume fraction may range from the lower limit,

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for a fully dispersed system, to the upper limit, for a colloidal gel. Accordingly, experimental reports of thermal conductivities that exceed the lower bound of the theory could likely be accounted for by the presence of colloidal clusters. In an extensive review of the experimental literature over the past 15 years, Eapen and coworkers showed that measured conductivities are found to lie between these two bounds.[14] The clustering hypothesis expands the range of thermal conductivities that are acceptable within the classical view, but this fact alone does not prove that clustering is indeed the mechanism responsible for enhancements that fall in this range. In fact, the aggregation state of the colloid was not controlled in the studies reviewed by Eapen *et al.*[14] The most direct evidence for the thermal effect of aggregated structures comes from dispersions of magnetic nanoparticles,[16,17] where it has been demonstrated that the conductivity of the dispersion increases monotonically with the applied magnetic field, due to the formation of linear chains along the magnetic lines. Linear chains, however, are not typical in usual colloidal systems, whose clusters tend to form fractal structures with fractal dimension in the range 1.8–2.5.[18] Apart from magnetic fluids, the ability of clusters and colloidal networks to increase the conductivity above that of the well-dispersed state has been predicted by simulation[5] and observed experimentally,[7,9,19] but the magnitude of the enhancement falls short of Maxwell's predictions.[19] The uncertainty that continues to surround the magnitude of the thermal conductivity of colloidal dispersions and the precise effect of clustering is due to the experimental difficulty in preparing systems whose aggregation state is well characterized and precisely controlled.

In this letter we show that clustering increases the conductivity of the dispersion and is capable of bridging the entire region between the two bounds of Maxwell's theory. To achieve control of the cluster size we have engineered a colloidal system that allows the production of colloidally stable clusters whose degree of clustering can be varied reversibly from the fully dispersed state to a colloidal gel. We fix the volume fraction of the primary particles and measure the thermal conductivity of the suspension as a function of cluster size to demonstrate systematic increases between the lower and upper bounds of Maxwell's theory. We produce well-controlled colloidal aggregates via chemical modification of colloidal silica. The details will be reported elsewhere but the main features of process are as follows. We begin with 30 nm (diameter) Ludox$^{TM}$ silica in water and graft onto their surface a silane, in this case *N*-[3-(trimethoxysilyl)propyl]ethylenediamine (TMPE). At pH $\lesssim$ 4, the amino groups are positively charged and result in a well-dispersed colloid stabilized by electrostatic repulsion. At basic pH the amino groups are neutral and the lack of repulsion, along with the hydrophobic interaction between the grafted chains and the aqueous environment causes aggregation and even gelling, if the volume fraction is sufficiently high. In the intermediate region the cluster size is set by the balance between electrostatic and hydrophobic interaction and is fully determined by pH. These transformations are reversible because the silanized surface prevents the silica particles from binding irreversibly. Thus by control of the pH this system can span the entire range from fully dispersed nanospheres to a percolated colloidal gel, and back. Using this process we produce dispersions with volume fraction in the range 11%–22% and measure the thermal conductivity as a function of cluster size using the hot wire transient method. Cluster sizes are measured by dynamic light scattering.

First we assess the effect of TMPE coating on the conductivity of silica. We functionalize silica with varying amounts of silane and measure the conductivity of dispersions at constant volume fraction $\phi_p = 22.4\%$ and pH = 4, such that the colloid exists in fully dispersed state. To avoid aggregation that invariably occurs when particles are dried and then redispersed, thermal conductivities are measured in the liquid medium that is obtained after reaction with the silane. This medium consists of mostly water with small amounts of methanol produced by the hydrolysis of TMPE. Its conductivity was measured separately and was found to range from 0.70 W/m K to 0.676 W/m K, depending on the amount of methanol. Figure 1 shows the conductivity of the dispersion as a function of the amount of TMPE. At concentration 0.05 g/ml of TMPE we obtain practically full coverage of surface hydroxyls, as determined by measurement of the zeta potential pH range 2–12, which matches the ionization behavior of the amino groups (positive potential at acidic pH, neutral in the basic region). The conductivity decreases with increasing silane coverage, indicating that the silane adds thermal resistance to the particle. The conductivity of organic molecules is generally low. Monoethyl amine, for example, has a conductivity of 0.240 W/m K,[20] about one
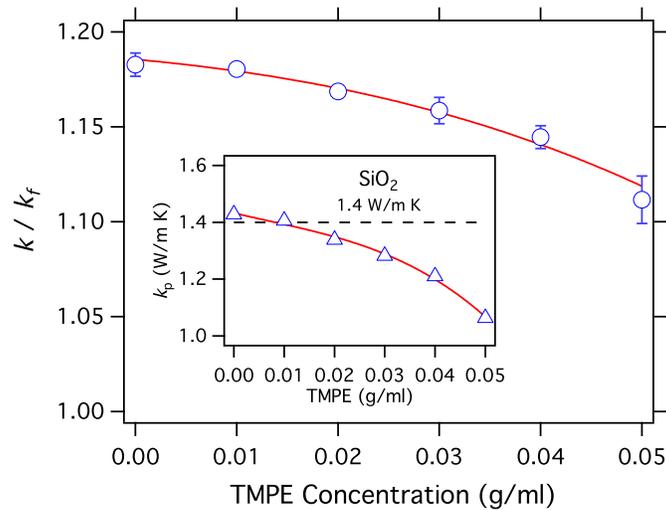
FIG. 1. Enhancement of the thermal conductivity of silane-treated silica suspensions as a function of the amount of silane at fixed volume fraction of particles $\phi_p = 22.4\%$. The inset graph shows the conductivity of the silane-treated silica particles, extracted from the conductivity of the suspension. The thermal resistance of the silane layer results in a 25% drop of the conductivity of the particle.
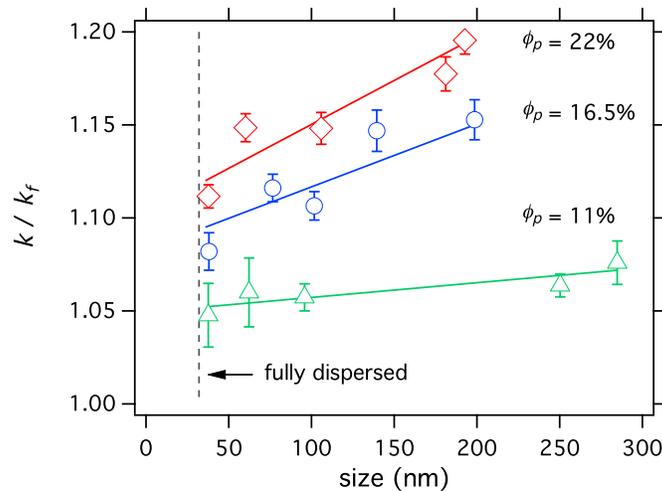


FIG. 2. Enhancement of thermal conductivity of aggregated nanoparticles. Each line represents a fixed volume fraction of nanoparticles. The dashed line marks the size of unmodified Ludox. Coated particles have a hydrodynamic radius that is 5 nm larger.

sixth of the conductivity of silica. It is therefore not surprising that a monolayer of surface silane has such strong effect on thermal conduction. We back-calculate the effective conductivity of the modified silica by solving the lower bound of Maxwell's prediction for $k_p$ at volume fraction $\phi_p$ = 22.4% using the measured conductivity $k_f$ of the base fluid. The results are shown in the inset graph in Fig. 1. At 0% TMPE we obtain $k_p = 1.43$ W/m K, in excellent agreement with the literature value $k_{SiO_2} = 1.4$ W/m K for silica,[14] indicating that the lower bound of Maxwell's theory is indeed obeyed in the fully dispersed state. At the other end, full surface coverage by TMPE reduces the conductivity of silica by 25%.

To study the effect of clustering we prepare suspensions of silanized silica at full surface coverage at three volume fractions, 11%, 16.5%, and 22%. At each volume fraction we adjust the pH to obtain clusters that range from 39 nm in diameter (fully dispersed) up to 300 nm, as measured by dynamic light scattering. The conductivity of the suspension is plotted in Fig. 2 as a function of
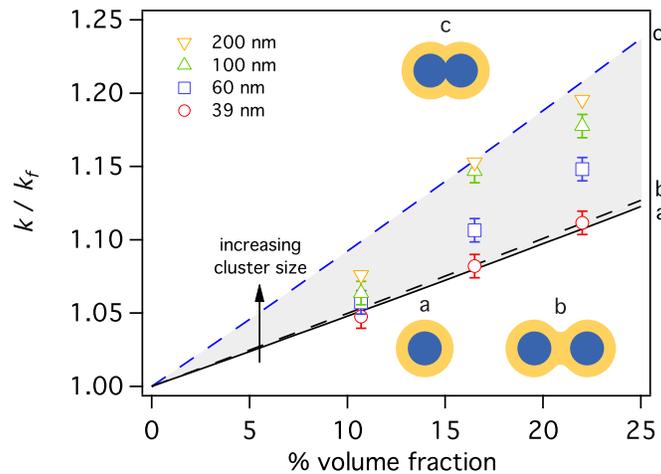
FIG. 3. Enhancement of thermal conductivity of aggregated nanoparticles as a function of the volume fraction of silica (size of aggregates increases in the direction of the arrow). (a) Lower Maxwell bound based on conductivity of modified silica; (b) upper Maxwell bound assuming the silane coating to form a low-conductivity solid shell that prevents thermal contact between silica cores; and (c) upper Maxwell bound assuming that silane coating permits thermal contact between silica cores.

cluster size. The conductivity increases approximately linearly with increasing aggregate size and the effect is more pronounced at higher volume fractions. At $\phi_p = 0.22$, for example, the conductivity of the dispersion nearly doubles as the cluster size is increased from 39 nm to 200 nm. The results follow qualitative trends that have been reported previously.[16, 17, 19] We now examine this behavior in quantitative terms, in the context of Maxwell's theory, by replotting the data as a function of the volume fraction of the primary particles as shown in Fig. 3. Here, each data set represents contours of constant cluster size at fixed volume fraction, obtained from the data in Fig. 2. The lines marked (a) and (b) show, respectively, the lower and upper bounds of Maxwell's theory calculated with $k_p = 1.063 \, \text{W/mK}$, corresponding to the decreased conductivity of silane-coated silica. The corresponding solid-to-fluid ratio of conductivities, $k_p/k_f = 1.56$, is too close to 1 and produces an extremely narrow range between the lower and upper limit of the theory. For this system, theory predicts no appreciable effect of cluster size. This is at odds with the experimental results. While this apparent conflict seems to suggest "anomalous" enhancement, we show that this is not the case.

The upper limit, labelled (b) in Fig. 3, treats the silane layer as a rigid film whose poor thermal properties make it an insulator that decreases the effective conductivity of the particle. Clusters make contact at the surface of the insulating layer and the chains they form are poor conductors because the most conductive phase, the silica core of individual spheres, remains isolated inside the insulating phase (shown schematically by the doublet labelled (b) in Fig. 3). In reality, the silane layer is neither rigid, nor does it provide a complete physical barrier over the solid core. It consists of short flexible chains that are attached to surface hydroxyls, while leaving silicon and oxygen atoms that belong to surface siloxane bonds exposed.[21] With all surface hydroxyls capped by the silane, the exposed surface is estimated to be approximately 50% of the total area.[22] In this picture, particles are capable of making thermal contact between silica cores even when silane is present such that their clusters form chains in which the continuous phase is the core material (depicted by the doublet labelled (c) in Fig. 3). The conductivity of these chains is clearly higher than that predicted under the assumption of no thermal contact between silica cores (line (b) in Fig. 3). In fact, the thermal behavior of these clusters is expected to be much closer to that of unmodified silica because thermal transport is dominated by the conductivity of the core material, whereas the resistance of the silane layer matters only at the entry and exit points of the heat path through the solid network. According to this model, we expect the conductivity of the clusters to reach as high as the upper limit of Maxwell's theory for unmodified silica. This limit is shown by the line labelled (c) in Fig. 3. The experimental data are seen to span the entire region between the two bounds of the theory. More importantly, the largest clusters approach very close to the upper limit of the theory.
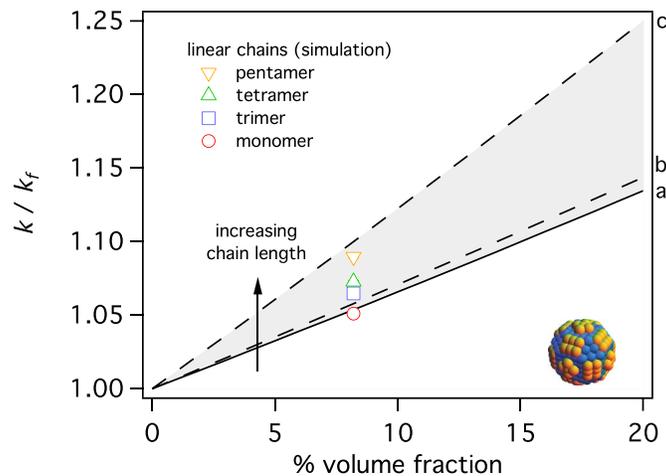
FIG. 4. Numerical simulation of the conductivity of dispersion composed of clusters of patchy spheres. The Maxwell bounds labelled (a)–(c) are the same as in Fig. 3. The patchy particle is shown on the bottom right corner, with each sphere representing a Monte Carlo lattice site of either silica (blue) or silane (yellow).

We test this interpretation by numerical calculation. We model silanized silica as a spherical core that contains surface patches of silane domains that cover 34% of the particle surface. The conductivity of the core is set to $k_p/k_f = 2.5$, whereas the conductivity of the patches is set to half that of the core ($k_{silane}/k_p = 0.5$), resulting in a decrease of the conductivity of the coated particle by 29%. These values closely match those in the experiment but are somewhat higher to avoid difficulties associated with larger numerical error when $k_p/k_f \rightarrow 1$. We form dispersions of single spheres and linear chains ranging from trimers to pentamers, and calculate their thermal conductivity by Monte Carlo.[23] We discretize each particle into 787 volume elements (shown as small spheres in the inset image in Fig. 4) with 102 of them representing silane patches on the particle surface (shown in gold). A single particle or chain placed inside a cubic lattice whose size is adjusted to produce a volume fraction $\phi_p = 8.2\%$, the surrounding space is filled with a fluid, also represented by discrete volume elements, and the conductivity of the system is calculated using the method of DeW. Van Siclen.[23] According to this method, a number of walkers are launched on a random walk that is biased by the conductivity of the local site. The conductivity of the simulated dispersion is obtained from the evolution of the mean-squared displacement of the walk.

The results of this calculation are shown in Fig. 4 along the predictions of Maxwell's theory. The lower bound (a) and upper bound (b) are calculated using the conductivity of a silane covered particle ($k'_p/k_f = 1.775$), whereas case (c) is the upper limit for the unmodified particle ($k_p/k_f = 2.5$). The fully dispersed spheres are in excellent agreement with the lower bound of the theory. Upon increasing the length of the chains formed by these patchy particles, the conductivity increases systematically and approaches the upper limit of the theory. The pentameric chain is the largest linear cluster that can fit into the simulation volume. This chain forms a continuous conducting path between two opposing faces of the simulation volume and reaches to within 89.5% of the upper limit of the theory. These calculations are in agreement with the experimental observations and confirm that the thermal behavior of silane-treated silica is upper-bounded by the conductivity of unmodified silica, and that this bound can be reached if the size of the clusters is sufficiently large.

This study answers unambiguously the question as to the effect of clustering on the thermal conductivity of colloidal dispersions. This effect is strong and gives rise to conductivities in the entire region between the two classical limits of Maxwell's theory. This demonstrates that the conductivity of nanocolloidal systems can be understood completely within the classical view, as suggested by Keblinski et al.[24] and Eapen et al.[14] While this does not preclude the prepense of other mechanisms that are microscopic in nature, their effects cannot be assessed experimentally unless the colloidal state of the system is controlled. The practice of producing suspensions by dispersing dry powders in a base fluid under stirring and sonication is inadequate because the presence of aggregates can

be neither avoided nor controlled. Equally important is the observation that thermal conductivity is very sensitive to the chemistry at the particle surface. Even partial coverage of the silica surface by silane produces a measurable drop in the conductivity of the particle. Surfactants and other common additives likely have a similar effect, therefore, their use in thermal applications must be assessed. The surface effect is not necessarily a detriment and could also be engineered to produce a colloid with improved thermal properties. If one deposits a highly conductive material as a surface layer on a core particle that is not necessarily a good conductor, the resulting system would be a better thermal medium than either the core particle alone, or a well-dispersed colloid made of the highly conductive material. This follows directly from Maxwell's classical theory (upper limit in Eq. (1)), which shows that an inhomogeneous two-phase system exhibits its highest conductivity when the more conductive phase surrounds the one that conducts less.

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