Research Article

Effect of Nanostructure on Thermal Conductivity of Nanofluids

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The presence of colloidal particles is known to increase the thermal conductivity of base fluids. The shape and structure of the solid particles are important in determining the magnitude of enhancement. Spherical particles—the only shape for which analytic theories exist—produce the smallest enhancement. Nonspherical shapes, including clusters formed by colloidal aggregation, provide substantially higher enhancements. We conduct a numerical study of the thermal conductivity of nonspherical structures dispersed in a liquid at fixed volume fraction in order to identify structural features that promote the conduction of heat. We find that elongated structures provide high enhancements, especially if they are long enough to create a solid network (colloidal gel). Cross-linking further enhances thermal transport by directing heat in multiple directions. The most efficient structure is the one formed by hollow spheres consisting of a solid shell and a core filled by the fluid. In both dispersed and aggregated forms, hollow spheres provide enhancements that approach the theoretical limit set by Maxwell's theory.

1. Introduction

Common fluids used in heating/cooling processes have very low thermal conductivity in comparison to solid materials [1]. Adding nanoparticles results in considerable improvement of the fluid thermal properties [2, 3]. While solid particles of any size will increase the thermal conductivity of the base fluid, there is a great interest in nanoparticles due to practical considerations associated with the production of stable suspensions that resist precipitation. Adding to this practical concern is a number of experimental reports of unusually large but often inconsistent increases of the thermal conductivity when working with nanoparticles [3], which have motivated various hypotheses as to the microscopic origins of these behaviors [4, 5]. Large enhancements of the thermal conductivity have recently been associated with aggregation [6–8]; however, analytical theories are not equipped to address the conductivity of aggregated structures quantitatively. The standard theoretical tool for conduction in inhomogeneous media such as colloidal dispersions is Maxwell's mean field theory [9]. Maxwell's result, originally developed in the context of electrical conduction, gives the

conductivity of a dispersion of spheres in a continuous medium:

$$k = k_f \frac{2k_f + k_p + 2\phi_p(k_p - k_f)}{2k_f + k_p - \phi_p(k_p - k_f)}, \quad (1)$$

where k is the conductivity of the dispersion, k_p is the conductivity of the particles, k_f is the conductivity of the fluid, and ϕ_p is the volume fraction of the particles. As the conductivity of solids is typically higher to much higher than that of liquids, this equation predicts that the conductivity of the dispersion is higher than that of the fluid. An even higher conductivity is obtained if the roles of the solid and liquid are inverted to produce a dispersion of liquid droplets inside a continuous solid matrix with the same volume fraction. The result is obtained by swapping k_p and k_f in (1) and replacing ϕ_p by $1 - \phi_p$:

$$k' = k_p \frac{k_f(3 - 2\phi_p) + 2\phi_p k_p}{k_f \phi_p + k_p(3 - \phi_p)}. \quad (2)$$

Equations (1) and (2) establish two limits for the thermal conductivity of an inhomogeneous system composed of two

phases at fixed volume fraction. The lower limit, (1), refers to a dispersion of the more conductive phase in a medium of low conductivity, whereas (2) refers to a dispersion of the less conductive phase in a continuum formed by the more conductive phase. Eapen et al. [7] suggested that (2) can be viewed as an upper limit for a colloidal gel, whose structure consists of a continuous solid network with regions of liquid dispersed in the interior. The two bounds may be taken then to represent the limits of fully dispersed particles (lower limit) and a fully gelled colloid (upper limit), with finite clusters falling in the space between these bounds. Recently, Lotfizadeh et al. [8] confirmed this hypothesis by showing that the thermal conductivity of a suspension at fixed volume fraction of primary particles increases monotonically with cluster size and reaches the upper limit of Maxwell's theory in the gel state. In a subsequent study, this behavior was quantified via an analytic model based on Maxwell's theory [10]. This model, however, depends on a parameter that reflects the structure of the cluster and which cannot be obtained by analytic means.

Structural details of colloidal clusters are important in determining the conductivity of the dispersion. While Maxwell's theory provides a baseline calculation for two idealized limits, that of fully dispersed and that of fully gelled states, for nearly all other cases theory is inadequate and one must resort to numerical simulations. To evaluate thermal conductivity of colloidal suspensions with different properties including particles shape and size along with investigating the effect of aggregation and cluster structure using model configurations, we need to go beyond experimental limitations and employ an accurate numerical model to avoid colloidal complications. In macroscopic simulations, large-scale structural effects can be captured. These simulations can be done by different standard models to solve the macroscopic conduction equation; however Monte Carlo method is both fast and accurate and especially well suited for complex geometries.

In this study we present a systematic investigation on the thermal conductivity of nonspherical particles with special interest in identifying structures that maximize conductivity at fixed volume fraction of the solid and approach the upper limit of the theory. We explore the range of validity of Maxwell's theory for different particle shapes, evaluate thermal conductivity of solid particles, hollow particles as well as rods, and other nonspherical shapes, and identify the structures that produce maximum enhancement at fixed volume fraction of the dispersed phase.

2. Monte Carlo Method for the Thermal Conductivity of Clusters

Of the several methods available for the conductivity of heterogeneous structures, Monte Carlo is particularly useful because it allows the study of systems with arbitrarily complex geometries. In Monte Carlo we obtain the thermal conductivity of a two-phase system via the statistics of a biased random walk along sites with different thermal conductivities. The method as implemented here ignores the motion of the

particle through the fluid medium as well as all fluid-mediated interactions between particles. We justify omitting these factors for two reasons. The first one is that Maxwell's theory itself only considers conduction and neglects all other mechanisms of heat transfer. In this respect the simulation provides a direct comparison to the predictions of Maxwell's theory. The second reason is based on the previous experimental and theoretical studies that show the enhancement of the thermal conductivity of clustered dispersions is fully captured by the conduction of heat along the solid backbone of the cluster and that other mechanisms, if present, make contributions that are at best within the error bounds of the experimental measurements [6–8, 10–13].

The Monte Carlo method used here is based on the work of Van Siclen [14]. The volume of the system (cluster in a fluid) is discretized in cubic elements of equal size, each element representing either fluid or particle. Heat walkers are launched randomly inside the system and take unit steps in one of 6 directions that exist in the discretized 3d lattice chosen at random. Movement of the walker is biased by the conductivity of the sites the walker is leaving from and moving to with transition probability:

$$p_{i \rightarrow j} = \frac{k_j}{k_i + k_j}, \quad (3)$$

where k_i is the conductivity of the current site and k_j the conductivity of the neighbor. Time is advanced by $1/k_i$ and the process is repeated to produce a trajectory in time, $\mathbf{r}(t)$. The thermal diffusivity D of the composite material is obtained from the Einstein relationship [15]:

$$D = \lim_{\tau \rightarrow \infty} \frac{1}{6t} \langle |\mathbf{r}(t + \tau) - \mathbf{r}(t)|^2 \rangle, \quad (4)$$

and the conductivity is finally calculated from its relationship with the thermal diffusivity, $k = \rho C_p D$, where C_p is the heat capacity. The implementation of the method is straightforward even for very complex solid structures and has been used by many others in the study of the thermal conduction in inhomogeneous media [15–19].

The dimensionless parameter that controls the conductivity of the suspension is the ratio of the solid-to-liquid thermal conductivity. Oxide materials in typical fluids have conductivity ratios in the range 2–50, and metallic particles can reach values of the order of 100. The ratio $k_p/k_f = 1$ is trivial and in this case the conductivity of the suspension is identical to that of the fluid for all particle structures and solid volume fractions. In the limit $k_p/k_f \rightarrow \infty$, heat conduction is entirely governed by the least conducting phase (liquid) and is independent of the conductivity of the solid [10, 20]. In this study we use ratios in the range 2 to 50, roughly corresponding to a range between aqueous dispersions of silica (lower limit) and alumina (upper limit). The results are qualitatively very similar to other ratios.

3. Results and Discussion

3.1. Validation of Numerical Simulation against Maxwell's Theory. An important element of the simulation is the discretization size of a unit element relative to the size of the spherical

FIGURE 1: Effect of the number of lattice sites: a single spherical particle is composed of numerical simulations on thermal conductivity of the suspensions with $k_p/k_f = 20$ at constant solid volume fraction of $\phi_p = 0.1$. The dashed line represents conductivity predicted by Maxwell's theory.

particle. In general, the smaller the discretization size, the more accurate the simulation but also more computationally intensive. It is common to represent primary solid particles by a single lattice site [11, 21]; however, the numerical accuracy of this simplification has not been reported in the literature. Thus the first test is evaluating the thermal conductivity of a single sphere within a unit lattice as a function of the discretization size. The results are shown in Figure 1. As the number of sites increases, the thermal conductivity of the dispersion, reported as a ratio over the conductivity of the fluid (we refer to this ratio as enhancement), increases and converges to the value predicted by Maxwell's theory. The most coarse representation of the sphere by a single lattice site underestimates the conductivity of the dispersion by 7%. Approximating the sphere with 7 sites (three orthogonal rows of 3 sites, each with a common center) produces results with the same accuracy as a sphere composed of 100 sites. In all subsequent simulations we use at least 7 lattice sites to represent each primary particle. As further validation we compute the conductivity of the dispersion as a function of volume fraction up to a maximum fraction of 25%, shown in Figure 2. These results are in excellent agreement with Maxwell's theory and further corroborate the findings of Belova and Murch [21] who reported very good agreement between simulation and Maxwell's theory for all volume fractions up to the point that particles begin to touch.

Figure 3 shows the conductivity of a dispersion at fixed volume fraction of solid as a function of size of the dispersed particles. The smaller particles are made of less primary lattice sites with maintaining the minimum sites required to keep the simulation accurate. The conductivity in all cases is the same and independent of the size of the dispersed spheres. This behavior, an important element of Maxwell's theory, is reproduced accurately by the simulation. We also show results for a dispersion of cubical particles at the same volume

FIGURE 2: Comparison of thermal conductivity between simulations (points) and Maxwell's theory (dashed line) for a well-dispersed suspension of spherical particles at different volume fractions with $k_p/k_f = 4$. The dispersion consists of spherical particles each represented by 7 lattice sites.

FIGURE 3: Effect of particle size of spherical particles on thermal conductivity of the solution at fixed volume fraction of $\phi_p = 0.05$ and $k_p/k_f = 4$. (a), (b), and (c) refer to spherical particles with different sizes at fixed volume fraction; (d) is a dispersion of cubical particles with the same volume fraction. The dashed line is Maxwell's theory for spheres.

fraction and observe that their thermal conductivity is within error indistinguishable from that of spherical particles.

3.2. Hollow Particles: A First-Order Model for Clusters. Maxwell's original derivation is based on a concentric core-shell model in which the core represents one phase (the dispersed solid) and the shell the other one (liquid) [9]. Maxwell showed that this arrangement has the same conductivity as a dispersion of spheres with the same volume fraction, a result confirmed in Figure 3. The upper bound of Maxwell's theory is obtained by inverting the order of the phases; the least conducting phase is now in the core and the most

conductive one in the shell. This allows us to calculate the conductivity of a suspension of *hollow* particles consisting of a solid shell and a core that is filled with the suspending fluid. The conductivity of a dispersion of hollow particles is calculated analytically from Maxwell's theory. First, the conductivity of a single hollow particle with outer and inner radii R_0 and R_i , respectively, is obtained from Maxwell's upper bound, (2), with ϕ_p being replaced by the solid fraction in the hollow particle, $\phi_i = 1 - (R_i/R_0)^3$:

$$k_h = k_p \frac{k_f (3 - 2\phi_i) + 2\phi_i k_p}{k_f \phi_i + k_p (3 - \phi_i)}, \quad (5)$$

where ϕ_i is the volume fraction of solid material inside the hollow particle. The conductivity of a dispersion of these hollow spheres at bulk volume fraction ϕ_h (based on the outer radius R_0) is given by the lower bound of Maxwell's theory with k_p being replaced by k_h and ϕ_p by ϕ_h :

$$k = k_f \frac{2k_f + k_h + 2\phi_h (k_h - k_f)}{2k_f + k_h - \phi_h (k_h - k_f)}. \quad (6)$$

The hollow sphere represents the simplest model of a colloidal cluster. This model views the cluster as a "microgel" structure consisting of an extended solid network that is modeled by the solid shell and pockets of liquid within the cluster that are represented by the core.

To test (6) by simulation, we calculate numerically the conductivity of a dispersion of hollow spheres at a fixed volume fraction of solid $\phi = 0.0656$ with $k_p/k_f = 20$ as a function of the ratio R_i/R_0 . With $R_i = 0$ we obtain a dispersion of solid spheres at volume fraction $\phi_p = 0.0656$. As we increase the outer radius the thickness of the shell is decreased to conserve the total amount of solid and the corresponding volume fraction of the dispersed hollow spheres is $\phi_h = \phi/\phi_i$, corresponding to fixed volume fraction of the solid phase $\phi = 0.0656$. The results are shown in Figure 4. The theoretical conductivity increases starting from the lower Maxwell limit ($k/k_f = 1.1801$) for spherical particles at $\phi_p = 0.0656$, $k_p/k_f = 20$, to the upper Maxwell limit ($k/k_f = 1.868$) at $(R_i/R_0)^3 = 1 - \phi = 0.934$. The Monte Carlo simulation tracks this profile closely.

In inhomogeneous two-phase systems, thermal conduction is dominated by the phase that provides the longest uninterrupted paths to heat transport. Given two materials of different conductivities layered in a core-shell arrangement, maximum conductivity is obtained when the most conductive material surrounds the least conductive phase. The smallest possible conductivity is achieved by reversing this order. In fact, if the less conductive phase is a perfect insulator, a core-shell particle with the insulator fully encapsulated will still conduct heat, whereas the inverted structure (insulator on the outside) is a perfect insulator. Generalizing this principle, structures that place the most conductive phase at the exterior while shielding the less conductive phase are expected to produce enhanced thermal conductivity relative to uniform dispersion of the more conductive phase. The hollow sphere is an exact analytic model that bridges the

FIGURE 4: Thermal conductivity of hollow particles as the core radius increases while the volume fraction of the solid shell is constant at $\phi = 6.5\%$ with $k_p/k_f = 20$ (the maximum possible value of $(R_i/R_0)^3$ is $1 - \phi = 0.934$ and is reached when the entire fluid is encapsulated in the core of a hollow sphere). The line represents conductivity predicted by Maxwell's theory as explained in the text.

entire range of conductivities between the two bounds of Maxwell's theory. At the lower limit we have a colloidal system of fully dispersed spheres. The upper limit represents an idealized system in which the entire fluid is found inside the core of a single hollow sphere. Such system cannot be made experimentally using primary spherical particles as its building blocks. Nonetheless, one does not need to reach this limit exactly to achieve high conductivity. With $(R_i/R_0)^3 = 0.75$ (corresponding to a hollow particle whose core is 25% of the total volume and the shell is 75%), the conductivity of the suspension is $k/k_f \approx 1.79$, about 30% above the lower bound and within 60% of the upper limit. Therefore, significant enhancements can be achieved with structures that are within experimental reach.

3.3. Rods. Among the many other structures that have been studied, nanotubes and nanofibers are of special interest as model structures for nonspherical particles. They can be made out of materials with high thermal conductivity and their anisotropic shape makes them potentially excellent additives to thermal fluids [22–33]. Maxwell's theory fails to predict thermal behavior of these suspensions. For compact nonspherical particles, the most common model is that of Hamilton and Crosser [34], which is based on the work of Fricke [35]. This model modifies Maxwell's lower limit as follows:

$$k = \frac{(n-1)k_f + k_p + (n-1)\phi_p(k_p - k_f)}{(n-1)k_f + k_p - \phi_p(k_p - k_f)}. \quad (7)$$

The shape of the particle is incorporated into the parameter n , whose general form is

$$n = \frac{3}{\psi^a}. \quad (8)$$

FIGURE 5: Thermal conductivity of suspensions of rods with aspect ratios in the range of $L/2R = 0.5$ to $L/2R = 5$ and, therefore, shape factors between $n = 3$ and $n = 6$ in comparison to Maxwell's limiting bounds (dashed lines) at volume fractions of $\phi_p = 0.019$ and $\phi_p = 0.039$. The inset graph shows the comparison between these simulated values (point) and Hamilton's model (line).

Here, ψ is the sphericity of the particle, defined as the surface area of an equal volume sphere over the surface area of the particle. In [35] the exponent a is 1 for spheres, 2 for prolate ellipsoids, and 1.5 for oblate ellipsoids. It is noted, however, that the experiments of Hamilton and Crosser [34] were better described with $a = 1$ regardless of shape.

For nonspherical particles ($\psi < 1$) (7) gives conductivities that are higher than that of spheres. To study Maxwell's range of validity for asymmetric particles, investigating thermal behavior of these particles and also validating Hamilton's model, simulations were established on rods with different aspect ratios ranging from $L/2R = 0.5$ to $L/2R = 5$. The conductivity ratio in these simulations is $k_p/k_f = 10$ and rods are made of discretized cells.

The results in Figure 5 show that enhancement at fixed volume fractions of $\phi_p = 0.019$ and $\phi_p = 0.039$ depends on the aspect ratio of the rods and that as the aspect ratio increases (sphericity decreases), conductivity increases above Maxwell's lower limit. Elongated particles such as rods and fibers facilitate heat transport along their primary axis. Upon increasing the aspect ratio, conductivity along the main axis increases substantially, and even though transport along the other two axes is decreased, the overall conductivity of the suspension is higher than that of spheres at the same volume fraction. Maximum enhancement is reached when the rod becomes long enough to connect two opposite sides of the cubic lattice. In our simulations, this occurs at $L/2R = 5$. While the conductivity increases above that of the lower limit in Maxwell's theory, it stays below the upper limit, even when the rod makes thermal contact between opposite ends of the simulation volume. The simulation results are compared to Hamilton's model in the inset in Figure 5. Excellent agreement was observed with $a = 1$.

FIGURE 6: Effect of aggregation state and cluster configuration on conductivity enhancement. Thermal conductivity of different model aggregates at $k_p/k_f = 20$ and solid volume fraction of $\phi_p = 0.1$ are presented. The last bar of the chart represents a structure created from hollow particles with the same solid volume fraction as all other structures. Structures 5–8 make contact with opposite walls.

The general conclusion from these investigations is that Maxwell's lower limit can be employed for suspension of monomers as long as we have symmetric shaped particles such as cubes and spheres, including core-shell structures. Anisotropic shapes, such as rods, cylinders, and ellipsoids, enhance conductivity above Maxwell's lower limit. Nonetheless, the enhancement is always found to lie below the maximum limit of Maxwell's theory.

3.4. Linear and Nonlinear Aggregates. Colloidal particles are susceptible to aggregation, especially in nanofluids prepared by dispersing dry particles in the fluid. Clusters are more complex in structure than the cases considered so far because of the random nature of contacts between the primary particles that make up the cluster. As a result, clusters with the same size (e.g., hydrodynamic radius) can have quite different structures, for example, linear, packed, fractal, and highly cross-linked. Although many studies have investigated different ways to create assemblies with controlled geometries [36, 37], controlling cluster configuration is an experimental challenge. MC simulations on the other hand enable us to create model aggregates and investigate thermal conductivity of such systems. This capability provides not only a tool to find the exact conductivity in systems with complex structures and different sizes but also a way to investigate the effect of configuration and geometry in aggregated structures on the conductivity.

Figure 6 shows thermal conductivity of different model aggregates with $\phi_p = 0.1$ and $k_p/k_f = 20$. The first four bars of this figure show thermal conductivity of suspensions containing linear clusters ranging from monomers to pentamers. The linear pentamer is the largest linear aggregate to fit in the simulation volume and makes thermal contact between opposite sides of the simulation box. The other clusters are formed by cross-linking linear chains in various

symmetric forms. The Maxwell bounds are also marked in this figure, the lower limit corresponding to the conductivity of dispersed spheres (structure #1 in the graph). Conductivity increases as the linear dimension increases, with pentameric chains reaching a value that is about 20% above Maxwell's lower limit. As with rods, maximum enhancement is reached when the chain makes thermal contact between opposite sides of the simulation volume. While linear clusters can increase conductivity significantly, the maximum enhancement remains well below that maximum allowed by Maxwell's upper limit. The next level of structural complexity involves cross-linking between linear branches, shown as structures #5 through #7. The X-shaped cluster, formed by cross-linking two chains (structure 5) and a tetrahedral cluster with four branches emanating from a common link, offers marginally higher enhancement than the linear pentamer. Structure 7, formed by cross-linking three chains aligned along the x -, y -, and z -axes, provides higher enhancement that is 30% above the lower bound. This result is somewhat unexpected because this structure has higher concentration of mass at the center and is closer to the structure of a sphere compared to the other structures. Its enhanced conductivity suggests that while linear branches are important in providing long pathways for heat transfer, the density of cross-linking is important as well and provides a locally high density of the more conducting phase that distributes heat to the branches. The last structure (8) is identical to 7, but the primary particles are hollow spheres (the volume fraction of the solid phase is $\phi = 0.1$, as in all of the cases in this figure). Hollow spheres in a suspension, as we established already, provide higher conductivity compared to solid spheres with the same volume fraction of solid, a trait carried over to aggregated structures. Indeed, the aggregate formed by hollow spheres exhibits the largest enhancement of thermal conductivity, 35% above the lower limit of Maxwell's theory.

4. Conclusions

We have studied by systematic numerical simulation the effect of nanostructure on the thermal properties of nanofluids. At fixed volume fractions, spherical particles exhibit the lowest possible thermal conductivity. Structures formed by creating contacts between primary particles always have higher conductivity compared to fully dispersed spheres. Structural elements that contribute to enhanced conductivity are linear branches, which facilitate heat transport along uninterrupted paths, and cross-links, which help distribute the transport to multiple directions. Both elements are needed to produce large enhancements. Structures that encapsulate the fluid within regions that are more or less thermally isolated from the main fluid exhibit the maximum enhancement. The ideal structure is a solid spherical shell that is filled with the suspending fluid. Colloidal aggregates are reasonable approximations of this highly conducting structure. In all cases, the conductivity of the nanofluid is found to lie between the two limits of Maxwell's theory. This adds further support to the suggestion that both the unusually large conductivities that have been reported in some studies and the inconsistencies as to the precise magnitude of

the enhancement of the thermal conductivity of colloidal suspensions can be attributed to the presence of nonspherical particles/aggregates in the nanofluid.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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