

Thermal Conductivity of Nanoscale Colloidal Solutions (Nanofluids)

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Researchers have been perplexed for the past five years with the unusually high thermal conductivity (k) of nanoparticle-laden colloidal solutions (nanofluids). Although various mechanisms and models have been proposed in the literature to explain the high k of these nanofluids, no concrete conclusions have been reached. Through an order-of-magnitude analysis of various possible mechanisms, we show that convection caused by the Brownian movement of these nanoparticles is primarily responsible for the enhancement in k of these colloidal nanofluids.

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The research community has been thoroughly perplexed by the unusually high thermal conductivity (k) of nanoparticle-laden colloidal fluidic systems at very low volume fractions (<0.05) [1–4]. These colloidal solutions are commonly referred to as nanofluids. Traditional k models for composites, such as the Maxwell-Garnett (MG) [5] model, completely fail to explain the enhancement in k in nanofluids [6,7]. The MG model has been successfully applied for explaining the k of solid-solid composites at small volume fractions [5]. Another aspect which is confusing is that, for nanosized particles, the impact of interfacial resistance (R_b) should be pronounced, and would tend to decrease the enhancement in k of the composite system as compared to micron-sized particles [5]. Cahill and co-workers [8] experimentally measured R_b between nanoparticles and different fluids. The magnitude of R_b ranged from low ($\approx 0.77 \times 10^{-8} \text{ K m}^2 \text{ W}^{-1}$) to high values ($\approx 20 \times 10^{-8} \text{ K m}^2 \text{ W}^{-1}$). The thermal conductivity k of a composite for the MG model, for $k_m \ll k_p$ where k_m is the matrix conductivity and k_p is the particle conductivity, is given by [5]

$$\frac{k}{k_m} = \frac{(1 + 2\alpha) + 2\phi(1 - \alpha)}{(1 + 2\alpha) - \phi(1 - \alpha)}, \quad (1)$$

where $\alpha = 2R_b k_m / d$, ϕ is the particle volume fraction, and d is the particle diameter. Equation (1) shows that, for $\alpha > 1$, k is lower than k_m and will continue to decrease with increasing ϕ . Even for R_b as low as $\approx 0.77 \times 10^{-8} \text{ K m}^2 \text{ W}^{-1}$, the critical diameter ($\alpha = 1$) is approximately 10 nm for water-based nanofluids.

Various mechanisms and models have been proposed for explaining the enhanced k of nanofluids using various assumptions. A few groups have proposed that the enhancement is due to the ordered layering of liquid molecules near the solid particles [6,9]. The resulting thickness and conductivity of the ordered layer both had to be assumed to be very high to match the measured values of

k . All these conduction models based on the ordered liquid layer can only possibly contribute to the enhancement of k for very small nanoparticles ($<10 \text{ nm}$), as shown by Yu and Choi [6]; however, almost all the data available in the literature except one set [10] are for nanoparticles larger than 10 nm. Considering the unphysical assumptions made for the ordered monolayers of liquid, we discard this as a possible mechanism. Jang and Choi [11] suggested a model based on the convection caused by the Brownian movement of the nanoparticles. They arbitrarily defined a thermal boundary layer, δ_T , as $\delta_T = 3\delta_F / \text{Pr}$, where Pr is the Prandtl number and δ_F is the diameter of the base fluid molecule, assuming the existence of ordered nanolayer. This assumption has little justification, and basically means that they assigned a thermal conductivity of $3h\delta_F / \text{Pr}$ to the ordered nanolayer, where h is the heat transfer coefficient which they evaluated by assuming that the Nusselt number (Nu) is given as $\text{Nu} \approx \text{Re}^2 \text{Pr}^2$, where Re is the Reynolds number. This relation also has little justification as it was derived based on neglecting all the relevant terms in the Nu relation for flow past a sphere. Their model is basically the same as the liquid-layering model. Furthermore they assumed that $k = (1 - \phi)k_f + \phi h \delta_T$, i.e., a parallel model of heat transfer, which is absolutely not true for such small ϕ . They also assumed that ϕ of the liquid layer is the same as the particle ϕ , whereas in reality it will be much smaller. Koo and Kleinstreuer [12] considered the kinetic energy of the nanoparticles due to the Brownian movement and used an undefined function. Bhattacharya *et al.* [13] offered an explanation based on the existence of an interparticle potential between the nanoparticles; however, they used two empirical parameters.

After discarding the impact of the layering, we consider the effects of three other possible mechanisms for thermal energy transfer in nanofluids: (1) translational Brownian motion; (2) the existence of an interparticle potential; (3) convection in the liquid due to the Brownian movement

of the particles. We perform an order-of-magnitude analysis to show that local convection caused by the Brownian movement of the nanoparticles is the only mechanism which comes close to explaining the observed k enhancement. Another important point is that if the observed exceptional enhancements of k are due to the small size of the particles, then at large particle sizes k should be explained based on the traditional conduction-based theory (e.g., MG) of composites. Therefore, any model should be able to make a transition such that at small particle sizes some other mechanism dominates, and at larger particle sizes a simple conduction-based mechanism dominates. Other requirements for any model for k is that it should include the effect of R_b .

Since the particles suspended in the liquid are very small, Brownian movement of the particles is quite possible. The root-mean-square velocity (ν_N) of a Brownian particle can be defined as [12,14]

$$\nu_N = \sqrt{\frac{3k_b T}{m_N}} = \frac{1}{d_N} \sqrt{\frac{18k_b T}{\pi \rho_N d_N}}, \quad (2)$$

where k_b is the Boltzmann constant, T the temperature, m_N the particle mass, ρ_N the density, and d_N the diameter of the nanoparticle. Applying kinetic theory, the enhancement in k due to the Brownian movement of the particles can be written as $k_{\text{Brownian}} = (\phi C_N \nu_N l)/3$, where C_N is the heat capacity per unit volume of the nanoparticles, and l is the mean free path (MFP) due to the collision of the nanoparticles with each other and with the liquid molecules. As a first estimate l can be assumed to be the same as d_N , but as this does not consider the impact of particle-liquid interaction on the MFP, because in reality the MFP will be smaller than the diameter of the particles [11]. Assuming $\phi = 0.05$ and Al_2O_3 nanoparticles of size 10 nm, the observed enhancement in k for a water-based nanofluid can be shown to be 0.2%, and 0.5% for ethylene glycol (EG), which is too small to explain the observed k data.

Since these particles are very small, interparticle surface forces might become very important [15]. The existence of the interparticle forces may give rise to different energy modes for thermal transport. Assuming that the interparticle potential can lead to phononlike energy modes, an upper bound estimate can be made for the enhancement in k . Because of the interparticle potential the highest specific heat per unit volume is $3nk_b$, where n is the number of nanoparticles per unit volume. The enhancement in k by applying kinetic theory is $k = nk_b \nu l_p = (6\phi/\pi d_N^3) k_b \nu l_p$, where ν is the velocity of the phononlike mode and l_p is the MFP of these modes. Assuming that the interparticle potential is as strong as the potential between atoms in crystalline solids, ν for these modes is assumed to be on the order of 5000 m s^{-1} (sound speed in typical solids), and l_p is assumed to be 100 nm (typical for solids at room temperatures). The estimated enhancement in k for Al_2O_3

nanoparticles ($d_N = 10 \text{ nm}$, $\phi = 0.05$) can thus be shown to be 0.1% for water and 0.26% for EG. Even for this most optimistic case, this enhancement is negligible due to the very small number of nanoparticles per unit volume in the system.

Now we consider the effect of the convection of the liquid near the particles due to their Brownian movement. The Reynolds number based on ν_N given by Eq. (2) can be written as

$$\text{Re} = \frac{1}{\nu} \sqrt{\frac{18k_b T}{\pi \rho_N d_N}}, \quad (3)$$

where ν is the kinematic viscosity of the liquid. Note that Re for Brownian motion is inversely proportional to $d_N^{0.5}$. The Re for 10 nm Al_2O_3 nanoparticles in water, $\text{Re} = 0.029$, is very small and therefore for convection the flow falls in the Stokes regime. If a sphere is imbedded in a semi-infinite medium of thermal conductivity k_m , then Nu based on the radius of the particle ($a = d/2$) can be shown to be 1, i.e., $h = k_m/a$ [16]. In the Stokes regime h is given as [17] $h = (k_f/a)[1 + (1/4)\text{Re} \times \text{Pr}]$. Note these relations are derived analytically from first principles. This means that the effective k of the fluid due to the convection caused by the movement of a single sphere is

$$k_m = k_f[1 + (1/4)\text{Re} \times \text{Pr}]. \quad (4)$$

For a 10 nm Al_2O_3 nanoparticle, the enhancement at room temperature is approximately 4.2% for water and 6.6% for EG. Therefore the enhancement due to convection is one order of magnitude higher than any of the other mechanisms. Note that this is based on a single isolated sphere, whereas there will be interaction in the convection currents from different spheres (to be discussed later). Substituting Eq. (4) for k_m in Eq. (1), the effective k of the nanofluid can be written as

$$\frac{k}{k_f} = \left(1 + \frac{\text{Re} \times \text{Pr}}{4}\right) \left[\frac{(1 + 2\alpha) + 2\phi(1 - \alpha)}{(1 + 2\alpha) - \phi(1 - \alpha)}\right]. \quad (5)$$

Equation (5), together with the definition of Re given in Eq. (3), has all the necessary ingredients for predicting k , because it includes (1) conduction contribution of the particles, (2) R_b between the particles and the fluid, and (3) convection contribution (effective for smaller d_N). This model reduces to the MG model for larger particles, as Re goes to zero for larger particles. We call this model the single-sphere Brownian model (BM). So far we have not included any empiricism in the model. Figure 1 shows the comparison between the MG model and BM. For water R_b is assumed to be $R_b \approx 0.77 \times 10^{-8} \text{ K m}^2 \text{ W}^{-1}$ [8]. For EG there are no reported R_b measurements. The mechanisms for R_b between a liquid and a solid are not clear [8,18]. Molecular dynamics simulations [18] showed that R_b can vary greatly depending on the type of bonding between the liquid and the solid. Phonon-based diffuse mismatch model (DMM) predictions were within a factor

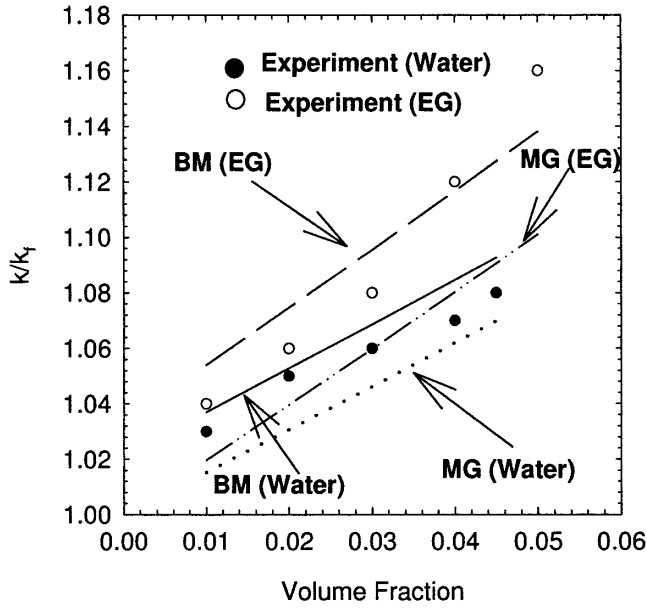


FIG. 1. Comparison of the Maxwell-Garnett and the single-sphere Brownian models with experimental data [1], for 38.4 nm Al_2O_3 nanoparticles at room temperature.

of 2 for different types of liquids [8]. An estimate for R_b for EG/solid is made based on DMM. According to DMM [19] $R_b = g(\nu_1, \nu_2)C^{-1}$, where g is a function of the sound velocity in the two media, and C is the heat capacity per unit volume. The velocity of sound in EG and water is approximately the same [20]. Therefore, we assume that $R_b(\text{EG}) = (C_{\text{water}}/C_{\text{EG}})R_b(\text{water})$ which gives $R_b(\text{EG}) \approx 1.2 \times 10^{-8} \text{ K m}^2 \text{ W}^{-1}$. Wilson *et al.* [8] also found experimentally that R_b for organic liquids was higher than the R_b for water. Figure 1 shows that the MG model underpredicts the data whereas it shows that, with no adjustable parameters, the simple single-sphere BM predicts the enhancement in k relatively well; however, this will not be the case in general due to the interaction of the convection currents from multiple particles.

The radial velocity field of a fluid due to the Stokes movement of a sphere is given as [21] $u_r = u_s - u_s[1 - 1.5(a/r) + 0.5(a/r)^3]\cos(\theta)$, where u_s is the fluid velocity at the surface of the sphere, r the radial distance from the surface of the sphere, and θ is the polar angle. Assuming the 99% criterion for the velocity to define the hydrodynamic boundary layer ($u_r = 0.01u_s$), the hydrodynamic boundary layer extends to $r/a \approx 50$. This shows that even at very small ϕ , the flow field due to two particles will interact and Eq. (4) thus needs to be modified. Heat transport in a nanofluid system is in some ways similar to particle-to-fluid heat transfer in fluidized beds, as convective currents from various spheres interact in fluidized beds [22]. Brodkey *et al.* [22] showed that for fluidized beds made of micron-sized particles, Nu for particle to fluid was 20–100 times more than that of the single-particle Nu. It is

also to be noted that, except for very simple conditions and geometries, the heat transfer correlations for convection in complicated situations such as those due to the presence of multiple spheres, are always empirical in nature [16,22]. Taking the cue from the Nu correlation for particle-to-fluid heat transfer in fluidized beds [22], we propose a general correlation for h of the form $h = k_f/a(1 + A\text{Re}^m\text{Pr}^{0.333}\phi)$ for the Brownian motion-induced convection from multiple nanoparticles, where A and m are constants. Convective heat transfer relations are regime dependent [16], and so depending on Re these relations can change. Therefore we think that most likely A should be independent of the fluid type whereas m will depend on the fluid type, as the properties of different fluids can vary dramatically (e.g., water and EG), which affects Re. This modification leads to

$$\frac{k}{k_f} = (1 + A\text{Re}^m\text{Pr}^{0.333}\phi) \left[\frac{(1 + 2\alpha) + 2\phi(1 - \alpha)}{(1 + 2\alpha) - \phi(1 - \alpha)} \right]. \quad (6)$$

If Eq. (6) is valid, then A and m should be the same for different experimental data for a particular fluid. Figure 2 shows the semiempirical model for k of various water-based nanofluids (different ϕ , d_N) assuming $R_b = 0.77 \times 10^{-8} \text{ K m}^2 \text{ W}^{-1}$. Except for the Al_2O_3 data from [1] and CuO data from [4], m was found to be 2.5 and $A = 40\,000$. For the data from [1], $m = 2.75$, and for the data from [4], $m = 2.4$ gave the best fit. Considering, however, the uncertainty in the value of R_b , the deviation of 10% in the value of m is very good. If $R_b = 2.5 \times 10^{-8} \text{ K m}^2 \text{ W}^{-1}$ and $0.25 \times 10^{-8} \text{ K m}^2 \text{ W}^{-1}$ are assumed for the data from

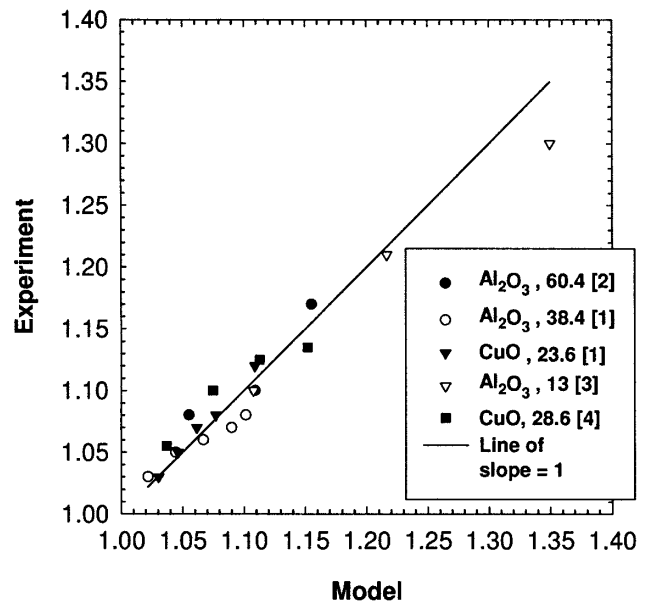


FIG. 2. Comparison of the semiempirical Brownian model with data. The number in the legend indicates the mean diameter of the particles, in nm.

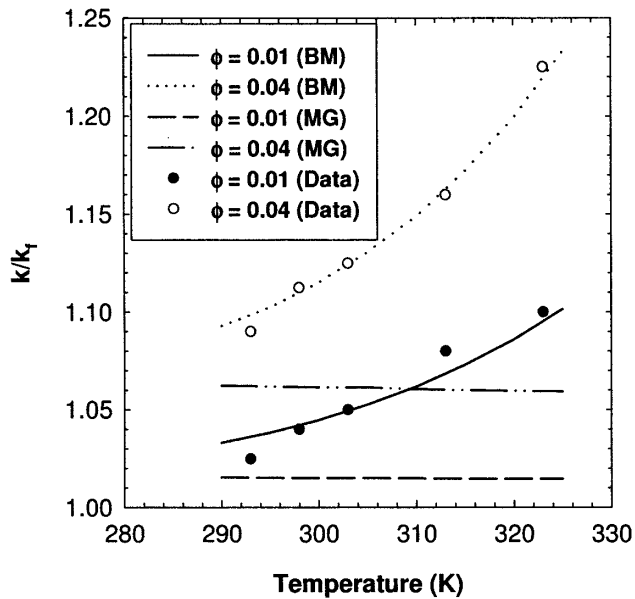


FIG. 3. Comparison of the semiempirical Brownian model with experimental data for 38 nm Al_2O_3 nanoparticles in water [4], for varying temperatures.

[1] (Al_2O_3) and [4] (CuO), respectively, $m = 2.5$ provides the best fit for all the data. Holman *et al.* [23] obtained $m = 2.0$ for water-based fluidized beds made of large particles, which is very close to the value of m obtained by us for the water-based nanofluids.

To test the validity of the proposed semiempirical model we applied it for experimental data obtained for k for different fluid temperatures [4]. Figure 3 demonstrates that, for $R_b = 0.77 \times 10^{-8} \text{ K m}^2 \text{ W}^{-1}$, the model matches very well with the data by assuming $m = 2.6$ and 2.4 for $\phi = 4\%$ and $\phi = 1\%$, respectively. The multiplier A was assumed to be the same as in Fig. 2 ($A = 40\,000$). If R_b were taken as a variable, then $m = 2.5$ matched the data for both 4% and 1% volume fraction, using $R_b = 1.5 \times 10^{-8} \text{ K m}^2 \text{ W}^{-1}$ and $0.5 \times 10^{-8} \text{ K m}^2 \text{ W}^{-1}$ for $\phi = 4\%$ and $\phi = 1\%$, respectively. Therefore, we think that $m = 2.5 \pm 15\%$ is the best value for m where water is the base fluid. It is to be noted that the variation in m could also be due solely to the experimental error in the measurement of k , or uncertainty in the mean d_N of the nanoparticles [1]. We have evaluated m based only on the reported values of k , and the reported mean d_N based on volume averaging. The variation in R_b due to various parameters, such as temperature, d_N , ϕ , and bonding, can also lead to uncertainty in the value of m . For EG we found that A is the same as that for water, as postulated in this Letter, and $m = 1.6$ gives a very good match for seven different experimental configurations. m has been found to depend on the type of fluids in fluidized beds [23], which is also consistent with our findings for the nanofluid system.

We have shown that convection due to the Brownian movement of the nanoparticles is the main reason for the

observed enhancement in k of nanofluids. We feel, however, that due to the convective nature of the heat transport any model will be semiempirical in nature, because of the complexities involved with the interaction in the convective currents due to multiple nanoparticles. To understand the exact origin of the empirical constants, it seems that a numerical simulation is needed. Such a numerical simulation would be different from typical particle or Stokesian dynamics. In addition to solving some form of the Langevin equation for the particle motions [13], the coupled Navier-Stokes and energy equations for the fluid also need to be computed. Another area which needs to be explored thoroughly is the origin, measurement, and modeling of R_b at a liquid/solid interface, for varying conditions.

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