

Mean-Field Versus Microconvection Effects in Nanofluid Thermal Conduction

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Transient hot-wire data on thermal conductivity of suspensions of silica and perfluorinated particles show agreement with the mean-field theory of Maxwell but not with the recently postulated microconvection mechanism. The influence of interfacial thermal resistance, convective effects at microscales, and the possibility of thermal conductivity enhancements beyond the Maxwell limit are discussed.

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Thermal conduction in a nanofluid (a colloidal suspension of nanosized particles) is a relatively recent topic of interest in colloidal science. The classical mean-field theory of Maxwell [1] appears to be at odds with several experiments which show significant thermal conductivity enhancements relative to the base fluid [2–5] and a strong size dependency [5–7]. A microconvection mechanism was postulated by Jang and Choi [8] and more recently by Prasher *et al.* [9] to explain this anomaly. It was hypothesized that convection currents set up by the Brownian motion of the nanoparticles could enhance the heat transfer between the nanoparticles and the base fluid, and hence the nanofluid thermal conductivity.

In this Letter, we present transient hot-wire (THW) measurements on aqueous suspensions of silica and perfluorinated nanoparticles, materials specifically selected for their low density and small intrinsic thermal conductivity. We find excellent agreement between the thermal conductivity data and the mean-field theory of Maxwell [1] for volume fractions up to 20%. The microconvection model [9], on the other hand, overestimates the thermal conductivity with an unphysical dependence on the nanoparticle density. We further show that this behavior arises from ascribing the nanoparticle thermal velocities as the convection velocities in place of the significantly lower thermophoretic drift velocities.

According to Maxwell [1], the thermal conductivity of a dilute suspension of well-dispersed spherical particles is given by

$$\frac{\kappa}{\kappa_f} = \frac{1 + 2\beta\phi}{1 - \beta\phi}, \quad (1)$$

where ϕ is the nanoparticle volume fraction, $\beta = [\kappa]/(\kappa_p + 2\kappa_f)$ and $[\kappa] \equiv \kappa_p - \kappa_f$ is the difference between the thermal conductivities of the nanoparticle and the base fluid. If a finite temperature discontinuity exists at the nanoparticle-fluid interface, Eq. (1) would still apply provided one makes the substitution $\kappa_f \rightarrow \kappa_f + \alpha\kappa_p$ (on the right-hand side), where $\alpha = 2R_b\kappa_f/d$, R_b is the inter-

facial thermal resistance, and d is the nanoparticle diameter [10,11]. In the microconvection model [9], it is argued that the Brownian motion of the nanoparticles is an efficient source of hydrodynamic convection. Assuming the Nusselt number on the scale of particle radius is $O(1)$, the Brownian motion of a single nanoparticle is regarded to increase the effective thermal conductivity of the base fluid by a factor of $[1 + (1/4)\text{Re Pr}]$, with Re and Pr denoting the Reynolds number for the nanoparticle and the Prandtl number for the base fluid, respectively. To account for the interfacial thermal resistance and the mixing of convection currents from multiple nanoparticles, the thermal conductivity of the nanofluid is fitted to the experimental data using the expression [9]

$$\frac{\kappa}{\kappa_f} = (1 + A\text{Re}^\gamma \text{Pr}^{0.333} \phi) \left(\frac{1 + 2\beta\phi}{1 - \beta\phi} \right), \quad (2)$$

where γ is a system-specific exponent, which for aqueous suspensions is found to have an optimal value of 2.5, and A is constant attaining values as large as 4×10^4 [9]. The hypothesized microconvection effects appear through $\text{Re} = Vd/\nu$, where V is the convection velocity and ν denotes the kinematic viscosity of the base fluid. In the microconvection model [9], the convection velocity is taken to be the root-mean-square (rms) velocity of the nanoparticle,

$$V = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{18k_B T}{\pi\rho d^3}}, \quad (3)$$

where T is the temperature, k_B is the Boltzmann constant, and m and ρ are the mass and density of nanoparticle, respectively. Two peculiar consequences of Eq. (2) are that for a given base fluid, temperature, and nanoparticle size, the enhancement in the thermal conductivity depends on the nanoparticle density ρ , and for nanoparticles with low density, the thermal conductivity can be largely positive even if $\kappa_p < \kappa_f$.

To test the prediction of the mean-field theory [Eq. (1)], and the density dependence of the microconvection model

[Eq. (2)], we have measured the thermal conductivity of spherical, colloidal suspensions made of amorphous silica (Ludox™ TMA, Grace Davison, USA), and MFA (Hyfon™, Solvay-Solexis, Bollate, Italy), a copolymer of tetrafluoroethylene and perfluoro-methylvinylether, (in what follows simply denoted as “Ludox” and “MFA”), respectively. Dynamic light scattering (DLS) and scanning electron microscope (SEM) measurements show that both kinds of particles are fairly monodisperse, with $d = 32 \pm 5$ nm for silica and $d = 44 \pm 2$ nm for MFA. Compared to inorganic colloids such as alumina and copper oxide, which thus far have been the subject of most thermal property investigations, these particles have a relatively low density ($\rho \sim 2200$ kg/m³ for Ludox, and $\rho \sim 2140$ kg/m³ for MFA) and thermal conductivity ($\kappa_p = 1.4$ W/mK for Ludox, and $\kappa_p = 0.2$ W/mK for MFA). Notice, in particular, that for MFA, κ_p is lower than that of water at room temperature ($\kappa_f = 0.61$ W/mK).

Measurements are performed using a custom-made THW setup. The THW method [12] consists of applying a constant current to a thin conducting wire, usually made of platinum, and measuring the time dependence of the wire electrical resistance, which is linearly related to the wire surface temperature. Provided some simplifying approximation are made, the thermal conductivity of the medium can be analytically related to the temporal evolution of the wire surface temperature [12]. Calibration measurements of water and water–ethylene-glycol mixtures have yielded thermal conductivity values within 3% of standard data over the temperature range 20–60 °C. We have also obtained data on stable dispersions of alumina nanoparticles in water which are in agreement with reported values in the literature. Additionally, we have performed numerical simulations of our experimental setup using the finite element solver FlexPDE™ (PDE Solutions Inc., USA), to confirm that natural fluid convection has negligible effects on the time scale of THW measurements (few seconds).

Our experimental results are delineated in Fig. 1 along with the predictions of the mean-field theory of Maxwell [Eq. (1)] and the microconvection model [Eq. (2)] [9]. The figure in the main body shows that the thermal conductivity of Ludox suspensions at room temperature (22 °C) grows linearly up to a particle volume fraction $\phi = 20\%$, displaying a slope that agrees with the Maxwell’s theory without invoking a finite interfacial thermal resistance. Strictly speaking, Maxwell theory is applicable in the dilute limit, $\phi \rightarrow 0$. However, it is also a limiting case of more rigorous theoretical bounds with finite volume fractions such as those stated by Hashin and Shtrikman (HS) [13]

$$\kappa_f \left(1 + \frac{3\phi[\kappa]}{3\kappa_f + (1-\phi)[\kappa]} \right) \leq \kappa \leq \left(1 - \frac{3(1-\phi)[\kappa]}{3\kappa_p - \phi[\kappa]} \right) \kappa_p. \quad (4)$$

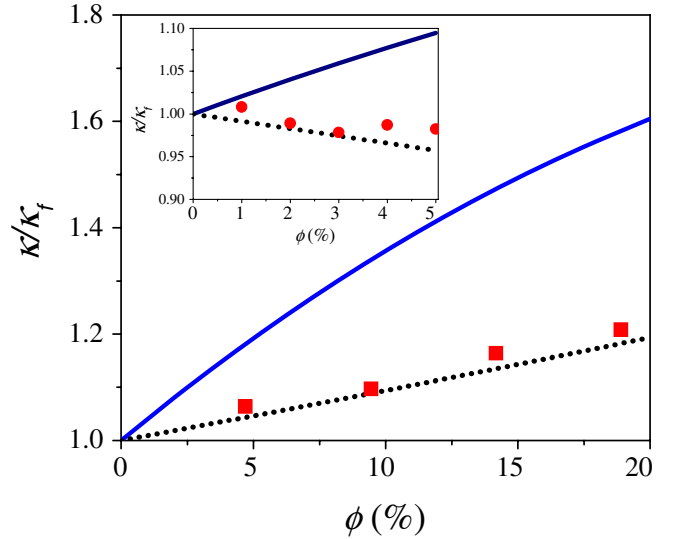


FIG. 1 (color online). THW data for the thermal conductivity of Ludox suspensions (squares) and MFA suspensions (circles) compared with the Maxwell model with $R_b = 0$ (dotted lines) and microconvection model [9] with $R_b = 2.5 \times 10^{-8}$ K m² W⁻¹, $\gamma = 2.5$, $A = 4 \times 10^4$ (solid lines). The uncertainty in the experimental data is within $\pm 3\%$.

We have assumed $\kappa_p > \kappa_f$ or otherwise, the upper and lower bounds would simply reverse. Notice that Eq. (1), which coincides with the lower HS bound when $\kappa_p > \kappa_f$ and with the upper bound in the opposite case, is rigorously exact to first order in ϕ , as evident from the dilute limit, $\kappa_p = \kappa_f(1 + 3\beta\phi)$. Physically, the upper HS bound corresponds to a nanocluster matrix with spherical inclusions of fluid regions while the lower HS bound assumes well-dispersed nanoparticles in the base fluid. The good agreement with the Maxwell theory suggests that the suspension may be envisioned as a static heterogeneous medium on the time scale of heat propagation.

The microconvection model [9] [Eq. (2) with $\beta = [1 - \alpha]/[1 + 2\alpha]$], on the other hand, clearly overestimates the thermal conductivity. We have used an interfacial resistance of $R_b = 2.5 \times 10^{-8}$ K m² W⁻¹, which is the largest value assumed in [9]. The inset in Fig. 1 shows that the mean-field description also accounts for the MFA data (at 22 °C) without any finite interfacial thermal resistance, albeit for this system the agreement is slightly poorer, possibly due to the larger uncertainty in the value for κ_p and to the narrower range of ϕ . The discrepancy with the microconvection picture is even more striking: While κ is found to decrease with ϕ (sensibly so, because $\kappa_p < \kappa_f$), the hypothesized microconvection predicts a nonphysical $d\kappa/d\phi > 0$. A good correspondence with Maxwell theory [Eq. (1)] is also obtained for the MFA particles in a wider range of ϕ (up to 20%) using optical thermal lensing measurements [14]. Regarding the sensitivity of the coefficients in the microconvection model, we note that even with $R_b \rightarrow \infty$, the microconvection model overpredicts the

experimental thermal conductivity by 15% for Ludox. Conversely, if γ is assumed to be a variable, a value of $R_b = 0.77 \times 10^{-8} \text{ K m}^2 \text{ W}^{-1}$ is found to be optimal [9]. However, an increase in γ from 2.5 to 2.7 overpredicts the conductivity by 20% for Ludox and also retains the non-physical positive enhancement for MFA. We would like to add that Eq. (2), as used in [9], has the limiting condition $\kappa_f \ll \kappa_p$, which is approximately satisfied for Ludox but not for MFA.

Our observations are better appreciated by noticing that Eq. (1) predicts κ_p/κ_f to be a universal function of $\beta\phi$ while the microconvection model [9] does not. In Fig. 2, we plot our two sets of data for Ludox and MFA as a function of $\beta\phi$ along with the reported experimental data in the literature for alumina [15] and copper oxide [15] which have higher densities as previously mentioned. Remarkably, all the experimental data collapse on to a single line predicted by the classical Maxwell theory ($R_b = 0$) regardless of the nanoparticle density (or size). However, assuming microconvection contributions lead to system-dependent predictions which are strongly conflicting with the experiments.

We will briefly comment on the role of interfacial thermal resistance effects, which have been frequently invoked to account for the apparent failure of the mean-field theories. The occurrence of an interfacial thermal (Kapitza) resistance at a liquid-solid interface has been experimentally evaluated by Cahill and co-workers [16] who observed a bounding R_b of $0.67 \times 10^{-8} \text{ K m}^2 \text{ W}^{-1}$ and $2 \times 10^{-8} \text{ K m}^2 \text{ W}^{-1}$ for hydrophilic and hydrophobic interfaces, respectively. Theoretical studies [17,18] also

show that R_b attains relatively large values only when the liquid does not wet the solid surface. In our context, complete wetting may be a reasonable assumption for dispersions of hydrophylic colloids such as Ludox, and possibly for charged MFA colloids, where particle solvation is ensured by electrostatic forces. Given the good correspondence between Eq. (1) and the experimental data in Fig. 2, and the relatively low values of R_b measured in experiments [16], the interfacial thermal resistance appears to play only a minor role in the thermal conduction behavior of nanofluids. More studies are, however, needed for a microscopic understanding of the solid-fluid interfacial resistance in the presence of solvation shells.

We will now analyze the key assumption of the microconvection mechanism in more detail, namely, that the random thermal (Brownian) motion of the nanoparticles will induce convective transport at microscales. Bulk motion of the fluid will appear as long wavelength modes of molecular motion [19] in the presence of externally imposed gradients such as pressure, gravity or temperature. A quiescent nanofluid (at equilibrium), therefore, will not support any convection regardless of Brownian motion of the nanoparticles. How does a thermal gradient modify this picture? Nonequilibrium coupling between mass and heat transport takes place due to the Soret effect [20]. For disperse systems, this means that a colloidal particle acquires a thermophoretic drift velocity $u_T = D_T \nabla T$ where D_T is the thermal diffusion coefficient [20]. Since the fluid molecules relax much quicker than the nanoparticles, on a time scale associated with the motion of the nanoparticles, the fluid molecules get dragged along with the nanoparticles depending on the level of slip velocity at the nanoparticle-fluid interface [21]. For nanoparticles, which are sufficiently larger than the molecular dimensions, the small Knudsen number [22] makes the no-slip interface conditions a reasonable approximation. Thus in typical thermal conduction experiments, the microconvection velocities are of the order of the thermophoretic velocities.

Compared to the magnitude of the strongly fluctuating thermal speed, the thermophoretic velocities are insignificant in a colloidal system. This is because the thermophoretic velocity is characteristic of the collective motion of fluid currents around several diffusing nanoparticles. Our optical thermal lensing measurements [14] have yielded a value of $D_T \sim 10^{-12} \text{ m}^2 \text{ s}^{-1} \text{ K}^{-1}$ for both Ludox and MFA colloids, which in typical THW experimental time scales corresponds to thermophoretic velocities as low as 1 nm/s while the rms velocities are $O(1)$ m/s. Using molecular dynamics simulations on a generic nanofluid, we have verified that the thermophoretic velocities are at least 2 orders of magnitude smaller than the thermal velocities even for particle sizes that are as small as 1 nm. The difference of several orders of magnitude in the convection velocities thus precludes a significant contribution from any conceivable microconvection mechanism to the ther-

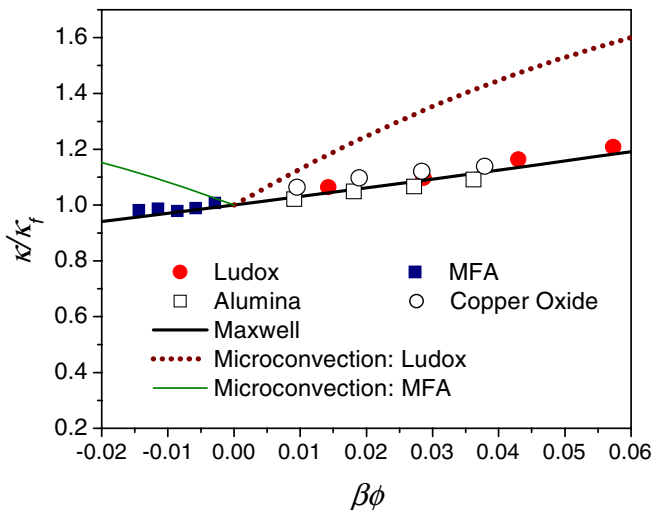


FIG. 2 (color online). THW data for Ludox ($\rho \sim 2200 \text{ kg/m}^3$, $d = 32 \text{ nm}$), MFA ($\rho \sim 2140 \text{ kg/m}^3$, $d = 44 \text{ nm}$), Al_2O_3 ($\rho \sim 4000 \text{ kg/m}^3$, $d = 38 \text{ nm}$) [15] and CuO ($\rho \sim 6300 \text{ kg/m}^3$, $d = 29 \text{ nm}$) [15] suspensions, plotted as a function of $\beta\phi$. The deviation of the microconvection model [9] from Maxwell for Al_2O_3 and CuO are comparable to the experimental uncertainty (results not shown).

mal conductivity. Our considerations here are consistent with the findings of Refs. [22,23] which show a negligible contribution of the moving particles to the nanofluid heat flux.

The question that remains unresolved is—Can a colloidal system have a thermal conductivity higher than that predicted by the Maxwell expression [Eq. (1)]? An answer to this question can help interpret the recent experiments which indicate unusually large enhancements (18%–25%) at very small volume fractions ($\leq 1\%$) [3–5]. Recent theoretical work has opened up two interesting possibilities [24–26]. If the nanoparticles form a linear chainlike agglomeration, then the thermal conductivity enhancement can exceed that of the Maxwell prediction through percolation [24,26]. This is a plausible mechanism for the experimentally tested nanofluids as the percolating paths favor a parallel mode of conduction and the thermal conductivity approaches the upper HS bound [Eq. (4)]. Indeed, all the published nanofluid data, with the exception of a few sets, fall between the upper and lower HS bounds, thereby manifesting the classical nature of thermal conduction in nanofluids. The other possibility is that a strong short-ranged nanoparticle–fluid attraction can lead to an enhanced thermal conductivity through the excess fluctuations in the potential energy [25] and phononlike (collision) conduction modes. For nanoparticles that are $O(1\text{ nm})$ in size, molecular dynamics simulations have shown that the fluid molecules form an amorphouslike interfacial structure around the nanoparticles that facilitates a percolating conduction network [27].

In conclusion, we have presented experimental evidence which indicates that microconvection of the fluid medium around randomly moving nanoparticles does not influence the thermal conductivity of a nanofluid. At the same time our experimental data are in good agreement with the Maxwell’s mean-field theory without invoking a finite interfacial thermal resistance. Our experiments and analysis however, do not preclude the possibility of having a larger thermal conductivity from chainlike clusters of nanoparticles [24], or from percolating interfacial fluid layers emanating from a strong nanoparticle–fluid attraction [25,27].

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