Optical measurements of the thermal properties of nanofluids

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The authors show that the thermal conductivity and diffusivity of colloidal particle dispersions can be rapidly obtained with high accuracy and reproducibility by exploiting a noninvasive, all-optical thermal lensing method. Applications of this technique to model suspensions of spherical monodisperse particles suggest that classical models for the effective properties of composite media hold up to rather high volume fractions, while no "anomalous" thermal conductivity effects are found. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2425015]

Efficient removal of excess heat from solid surfaces is a primary need in many productive sectors, ranging from the electronic to the nuclear industry. Unfortunately, when compared to solids, common thermovector fluids display rather poor thermal conductivity. A promising remedial strategy consists in dispersing highly conducting materials in the carrying fluid.[1] For instance, suspensions of nanometer-sized colloidal particles, now commonly dubbed "nanofluids," seem to substantially enhance the critical heat flux in pool boiling measurements, and have therefore been suggested as potential primary coolants in nuclear reactors.[2] The physical origin of this enhancement is, however, still debated. Most approaches have focused on an alleged "anomalous" increase of the thermal conductivity coefficient κ with respect to the solvent. Claims of a conductivity increase by 40%–50% for particle volume fractions Φ as low as $(2-3)\times 10^{-3}$ have indeed been made for copper[3] or carbon nanotube particle suspensions.[4] In addition, κ seems to show a striking and totally unexpected temperature dependence.[5] Yet, the experimental *status quo* is rather confusing, and conflicting evidences, reporting no or very weak anomaly, have been presented.[6] Such a rather unsatisfactory situation may be due to at least two kinds of reasons, namely, (i) most investigated systems are poorly characterized in terms of particle morphology, size distribution, and colloidal stability, and (ii) measurements are commonly performed using traditional methods such as the transient hot wire technique that may suffer from practical drawbacks due to convective effects[7] (which for aqueous samples may be more relevant at higher temperature). Attempts to overcome these limits led to exploring alternative investigation methods, such as the optical beam-deflection technique introduced in Ref. 6.

The purpose of this letter is twofold. First, we introduce an accurate all-optical method, based on "thermal lensing" effects, which allows simultaneous measurements of both the thermal conductivity and diffusivity $\chi=\kappa/\rho c$ (where ρ and c are the sample density and specific heat), while being virtually immune from spurious convective effects. We then investigate a model colloidal system made of monodisperse spherical particles, showing that, at least for this particular system, no "anomaly" is observed and that the observed behavior closely conforms up to high Φ values to the prediction of classical theories for thermal transport in heterogeneous media.

Thermal lensing (TL) is a self-effect on beam propagation taking place when a focused laser beam heats up a partially absorbing sample.[8,9] Thermal expansion of the absorbing medium induces a local density distribution that, close to the beam center, has a simple parabolic shape. Such a radial density gradient produces, in turn, a quadratic refractive index profile, acting as a negative lens that increases the divergence of the transmitted beam, which can be measured by detecting changes of the central beam intensity. Consider a Gaussian beam of wavelength λ and optical power P, focused to a beam waist w_0 into a sample with absorption coefficient b, refractive index n, and thickness l. Assuming that the sample is positioned at a distance $z=\sqrt{3}z_R$ from the beam waist, where $z_R=\pi w_0^2/\lambda$ is the Rayleigh range of the focused beam, and defining a dimensionless "thermal lens number" ϑ_{th} as

$$\vartheta_{\mathrm{th}} = -\frac{Pbl}{\kappa\lambda}\frac{\partial n}{\partial T}, \tag{1}$$

the time dependence of the central beam intensity is[10]

$$I(t) = I(0)\left[1 + f(t) + \frac{f(t)^2}{2}\right]^{-1}, \tag{2}$$

where $f(t)=\vartheta_{\mathrm{th}}\arctan(1/\sqrt{3})/(1+\tau_{\mathrm{th}}/t)$, and $\tau_{\mathrm{th}}=w_0^2/\chi$. This expression also takes into account aberrations of the thermal lens with respect to a simple parabolic approximation. Both the sample thermal conductivity and diffusivity can therefore be simultaneously obtained from the values of ϑ_{th} and τ_{th} derived from a fit of $I(t)$. An important distinction between suspensions and simple fluids is the possible occurrence for the former of particle thermophoresis (Soret effect), yielding an additional thermal lensing effect.[11] The latter, however, develops on a time scale set by the particle Brownian diffusion coefficient D, which is several orders of magnitudes smaller than χ, so that the purely thermal effect can be unambiguously singled out.

Our experimental setup has been specifically designed to work on aqueous suspensions by adopting as a source a fiber-coupled semiconductor laser operating at $\lambda=980$ nm, which coincides with a water weak vibrational band (absorption coefficient $b_s\simeq 0.5\ \mathrm{cm}^{-1}$). The collimated beam is focused by a lens into a thermostated cylindrical cell, with optical path $l=5$ mm, to a diffraction limited spot size $w_0\simeq 30\ \mu$m. The cell is micrometrically translated along the optical axis z until a maximal intensity change (which occurs at $z=\sqrt{3}z_R$) is found. Signal detection is made by a photodi-

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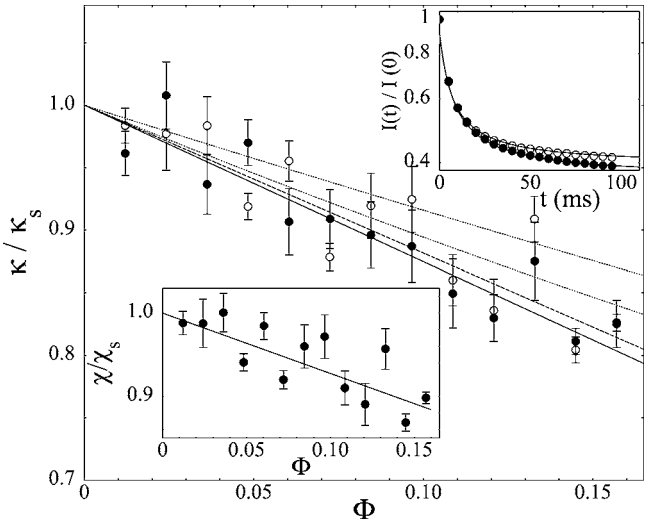

FIG. 1. Upper right inset: TL signals for a MFA suspension at $\Phi=0.157$ (•) compared to pure water (○). Full lines are fits using Eq. (2). Lower left inset: Thermal diffusivity of MFA suspensions obtained from τ_{th}. A linear fit yields $\chi/\chi_s=1-(0.71\pm0.06)\Phi$. Main body: thermal conductivity with respect to water for the same samples, obtained either from the thermal lens numbers ϑ_{th} (•) or from the thermal diffusivity data (○), using $\kappa=\rho c\chi$. The full and broken lines are linear fits to the data, while the two dotted curves correspond to the theoretical bound in Eq. (3).

ode, placed behind a pinhole selecting less than 0.5% of the beam spot area. The signal is then amplified, sampled at 200 kS/s, and eventually acquired and processed using a custom-made software. For a full description and discussion of our apparatus see Ref. 11.

To test our method, we have studied aqueous suspensions of spherical colloids made of MFA, a copolymer of tetrafluoroethylene and perfluoromethylvinylether (Hyflon™ MFA 1041, Solvay-Solexis, Bollate, Italy). The composing polymer has density $\rho_p=2.14$ g/cm^3, thermal conductivity $\kappa_p=0.2$ W/mK, and specific heat $c_p=0.9-1.1$ J/g K.[12] Dynamic light scattering measurements yield a particle average hydrodynamic radius $R=40$ nm, with a size polydispersity $\sigma\simeq6\%$. To avoid coagulation, the particles are stabilized by a 2 nm layer of the nonionic surfactant Triton X100. MFA colloids show very peculiar optical properties.[13] In particular, their refractive index $n=1.356$ is very close to that of water, so that the suspensions are fully transparent up to very high particle concentration. A series of samples was prepared by diluting a mother batch at $\Phi_0=0.157$, as determined by measurements of the solution density. All measurements were performed at $T=25$ °C. A precision Abbe refractometer was used to obtain $\partial n/\partial T$ as a function of Φ, yielding $\partial n/\partial T\simeq -0.98(1-0.45\Phi)\times10^{-4}$ K^{-1}. Since MFA does not absorb at 980 nm, the suspension absorption coefficient is simply given by $b(\Phi)=b_s(1-\Phi)$, while the specific heat of the suspension can be written as $\rho c=\rho_s c_s+(\rho_p c_p-\rho_s c_s)\Phi$.

The time dependence of the TL signals for the mother batch and for pure water are compared in the upper right inset of Fig. 1. Notice that the MFA suspension displays a larger thermal lensing effect, attesting to a stronger induced temperature gradient notwithstanding the *lower* value for the optical absorption coefficient of the dispersion $b(\Phi_0)=0.843b_s$. Therefore, the effective thermal conductivity decreases by adding MFA particles, as may be expected by observing that $\kappa_p<\kappa_s$. Yet, the low difference $\kappa_p-\kappa_s\simeq-0.4$ W/mK between the thermal conductivities of MFA and water yields rather modest changes of the TL signal even at $\Phi=\Phi_0$. The buildup time of the temperature field, derived from a fit with Eq. (2), is of the order $\tau_{th}\simeq10^{-2}$ s. In this time lapse, the Brownian rms displacement is only two to three particle diameters, while advective particle transport is totally negligible.[11] Within the experimental time frame, therefore, the system behaves as a composite medium where the particles are essentially frozen.

The results of our measurements are summarized in the main body of Fig. 1, where the ratio κ/κ_s is derived either directly, from the steady-state value of the detected intensity, or from the thermal diffusivity values $\chi=w_0^2/\tau_{th}$ obtained from the temporal dynamics of the TL signal, which are shown in the lower left inset. Notwithstanding the rather small change in κ, both sets of data display an approximately linear behavior up to the highest volume fraction, with slopes given by -1.25 ± 0.05 and -1.18 ± 0.06 for the steady-state and temporal dynamics values.

As opposed to the aforementioned status of the experimental research, theoretical results for the thermal properties of composite materials seem to be unambiguous (for a clear and comprehensive review, see Ref. 14). Maxwell seminal approach[15] (originally developed for the dielectric properties of heterogeneous media) yields, for a dilute suspension of spheres, an effective thermal conductivity given by $\kappa/\kappa_s=1+3\beta\Phi$, where $\beta=([\kappa])/(\kappa_p+2\kappa_s)$ and $[\kappa]=\kappa_p-\kappa_s$. This result can be generalized to different particle geometries, such as ellipsoids, fibers, or disks, by introducing opportune "concentration factors."[14] Extension to more concentrated suspensions is, however, far from being trivial. Effective field models yield the slightly corrected expression (already contained in Maxwell's original work) $\kappa/\kappa_s=(1+2\beta\Phi)/(1-\beta\Phi)$, but the range of validity of this result is unknown. Notwithstanding the lack of a general solution, rigorous upper and lower bounds for κ can, however, be stated. Hashin and Shtrikman[16] have shown that, *regardless* of the size, morphology, and volume fraction of the inclusions, the effective conductivity must satisfy

$$\bar{\kappa}-\frac{\Phi(1-\Phi)[\kappa]^2}{3\kappa_p-\Phi[\kappa]}\leqslant\kappa\leqslant\bar{\kappa}-\frac{\Phi(1-\Phi)[\kappa]^2}{3\kappa_s+(1-\Phi)[\kappa]}, \tag{3}$$

where $\bar{\kappa}=\kappa_p\Phi+\kappa_s(1-\Phi)$, and we have assumed $\kappa_p<\kappa_s$ (otherwise, the upper and lower bounds simply switch). With little algebra, it is also easy to show that the upper bound coincides with the effective field expression.

Comparing to our results, it is, first of all, surprising that linearity in Φ holds up to volume fractions where single particle models could be questionable. The simple Maxwell formula yields a slope $3\beta\simeq-0.86$, which is only about 30% lower in absolute value than our experimental result. Even more, all experimental data lie very close to the region bounded by the Hashin-Shtrikman limits. The residual small discrepancy may possibly arise from interfacial thermal resistance effects due to the presence of the surfactant stabilizing layer, or more probably to slight differences of the thermal properties of colloidal MFA from the bulk values.

Summarizing, we have shown that thermal lensing effects may be profitably exploited to measure the thermal properties of nanofluids, with the crucial benefit of avoiding artifacts stemming from particle diffusion or advection. The thermal conductivity of monodisperse spherical colloids closely abides to the theoretical predictions up to high Φ.

This does not, of course, exclude that particles with very high values of κ_p (or even more carbon nanotubes, where fiber entanglement may occur at very low Φ) may show meaningful anomalies. Yet, preliminary TL data we are collecting on suspensions of very small gold particles do not show pronounced effects. Whether or not a strongly enhanced thermal conductivity is the main cause of the observed increase of critical heat fluxes in nanofluids is yet to be further substantiated. We point out, however, that alternative explanations, stressing the promoting action of surface-deposited colloidal films in boiling heat transfer, have recently been proposed.[17]

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[1]P. Keblinski, J. A. Eastman, and D. G. Cahill, Mater. Today **8**, 219 (2005).
[2]S. M. You, J. H. Kim, and K. H. Kim, Appl. Phys. Lett. **83**, 3374 (2003).
[3]J. A. Eastman, S. U. S. Choi, S. Li, W. Yu, and L. J. Thompson, Appl. Phys. Lett. **78**, 718 (2001).
[4]S. U. S. Choi, Z. G. Zhang, W. Yu, F. E. Lockwood, and E. A. Grulke, Appl. Phys. Lett. **79**, 2252 (2001).
[5]S. K. Das, N. Putra, P. Thiesen, and W. Roetzel, ASME Trans. J. Heat Transfer **125**, 567 (2003).
[6]S. Putnam, D. G. Cahill, P. V. Braun, Z. B. Ge, and R. G. Shimmin, J. Appl. Phys. **99**, 084308 (2006).
[7]J. J. Healy, J. J. de Groot, and J. Kestin, Physica B & C **82**, 392 (1976).
[8]J. P. Gordon, R. C. C. Leite, R. S. Moore, S. P. S. Porto, and J. R. Whinnery, J. Appl. Phys. **36**, 3 (1965).
[9]J. R. Whinnery, D. T. Miller, and F. Dabby, IEEE J. Quantum Electron. **3**, 382 (1967).
[10]C. A. Carter and J. M. Harris, Appl. Opt. **23**, 476 (1984).
[11]R. Rusconi, L. Isa, and R. Piazza, J. Opt. Soc. Am. B **21**, 605 (2004).
[12]Solvay-Solexis, Technical Library, URL: http://www.solvay-solexis.com/pdf/Hyflon_MFA1041.pdf
[13]V. Degiorgio, R. Piazza, T. Bellini, and M. Visca, Adv. Colloid Interface Sci. **48**, 61 (1994).
[14]K. Z. Markov, *Heterogeneous Media: Modelling and Simulation*, edited by K. T. Markov and L. Preziosi (Birkauser, Boston, 2000), Chap. 1, p. 1.
[15]J. C. Maxwell, *A Treatise on Electricity and Magnetism*, 2nd ed. (Clarendon, Oxford, 1881), Vol. 1, p. 435.
[16]Z. Hashin and S. Shtrikman, J. Appl. Phys. **33**, 3125 (1962).
[17]S. J. Kim, I. C. Bang, J. Buongiorno, and L. W. Hu, Appl. Phys. Lett. **89**, 153107 (2006).