The role of several heat transfer mechanisms on the enhancement of thermal conductivity in nanofluids

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Abstract

A modelling of the thermal conductivity of nanofluids based on extended irreversible thermodynamics is proposed with emphasis on the role of several coupled heat transfer mechanisms: liquid interfacial layering between nanoparticles and base fluid, particles agglomeration and Brownian motion. The relative importance of each specific mechanism on the enhancement of the effective thermal conductivity is examined. It is shown that sizes of the nanoparticles and the liquid boundary layer around the particles play a determining role. For nanoparticles close to molecular range, the Brownian effect is important. At nanoparticles of the order of 1-100 nm, both agglomeration and liquid layering are influent. Agglomeration becomes the most important mechanism at nanoparticle sizes of the order of 100 nm and higher. The theoretical considerations are illustrated by three case-studies: suspensions of alumina rigid spherical nanoparticles in water, ethylene glycol and a 50/50 w% water/ethylene-glycol mixture, respectively, good agreement with experimental data is observed.

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1. Introduction

It has been shown that thermo-physical properties and in particular heat transfer coefficients of base fluids can be modified significantly by introducing nanoparticles [1, 2]. It is well-known that thermal conductivity of some nanofluids and nanocomposites is considerably enhanced by adding nanoparticles. A huge amount of theoretical work (e.g. [3, 4]), and experimental [5] works have been devoted to the subject. Most theoretical models are based on Maxwell's homogenization method [6, 7]. However, this approach does not take into account the particles size effect. This has led some people to formulate renovated Maxwell's models by introducing explicitly the particle's dimensions [8-12].

There has been recently much attention paid to some particular heat transfer mechanisms in nanofluids, such as formation of a nano-liquid-layer around the nanoparticles (liquid layering) [13-16], particles clustering [17-20] and Brownian motion of particles [21-23]. Contradictory conclusions have been formulated about the relative importance of the aforementioned mechanisms [1]. It is therefore the purpose of this work to shed more light on this matter. Several ways have been explored to study the change of thermal conductivity in nanofluids and nanocomposites like solving directly Boltzmann's transport equation for phonons [24], or constructing phenomenological models like those rooted on Maxwell's model [25] or mixing both macroscopic and microscopic considerations [11,12,26].

Because the size of the nano materials is comparable or somewhat larger than the mean free path of the heat carriers, heat transport is mainly of ballistic rather than diffusive nature; therefore Fourier's law is no longer valid and more sophisticated formulations are expected [27-29]. Here, we follow the line of thought of extended irreversible thermodynamics (EIT) [30-

33], which is a non-equilibrium thermodynamics theory especially suited to treat small-scale effects. The main idea underlying EIT is to upgrade the thermodynamic fluxes, like the heat flux to the status of independent variable at the same level as the classical variable, the temperature. The consequence is that Fourier's law will be substituted by more complex expressions allowing to deal with high frequency processes and small-scale systems. EIT has been applied in previous papers [12, 34] on heat transport in nanocomposites formed by spherical nanoparticles distributed randomly in diverse host matrices. The results were shown to be in good agreement with Monte Carlo simulations and other models using different schemes. In the following, we extend the previous developments about nanocomposites to nanofluids, which call for consideration of other heat transfer mechanisms, negligible in nanocomposites.

More specifically, we propose a mixt between Nan's renovated Maxwell model [8] known as the effective medium approximation (EMA) and Extended Irreversible Thermodynamics. Furthermore, the discussion is not limited to the description of the particular mechanisms of liquid layering, agglomeration and Brownian motion per se but emphasis is put on their coupling. This investigation is backed up by comparing the theoretical predictions with experimental data.

The paper is organized as follows. The mathematical model is set up in Section 2. It consists in a mixing of EMA and EIT. The main original part of the present work is Section 3 wherein is treated the interactive and combined influence of the heat transport mechanisms under study. In Section 4, the general analysis is particularized to the cases of alumina particles dispersed in water, ethylene-glycol and a 50/50 w% water and ethylene-glycol mixture, respectively. It is shown that the relative importance of each individual effect is mainly determined by the size of the nanoparticles and the thickness of the interfacial boundary layer. Supplementary comments are developed in Section 5 and conclusions are drawn in Section 6.

2. Mathematical model

Our objective is to derive a closed-form expression for the effective thermal conductivity of nanofluids in presence of various transport mechanisms. Thermal conductivity depends on several factors as the nanoparticles volume fraction, the thermal boundary resistance between fluid and particles and their shape and size. Here, for simplicity, the analysis is restricted to spherical rigid nanoparticles of the same dimension dispersed in a homogeneous fluid. The other working hypotheses are the following:

- particles are homogeneously dispersed,

- temperature is fixed equal to the room temperature,

- there is no electric surface charge,

- surfactants are absent.

Let us briefly comment about these hypotheses. The distribution of the dispersed particles is assumed to be uniform, i.e. independent of the spatial coordinates. Although it is true that concentration of particles is able to modify the heat conductivity, other factors like the ones investigated in this work play a more important role. At low volume fraction of particles and weak concentration gradients, the influence of the spatial distribution of particles on heat transfer is negligible due to the smallness of the coupling coefficients of the Soret and Dufour effects.

Modifying the temperature will of course influence the heat conductivity. It has been observed that increasing the temperature enhances generally the heat conductivity of nanofluids (e.g. [35, 36]). The assumption of a fixed temperature is motivated by the fact that most experimental data, to which we compare our theoretical results, are given at a fixed temperature. Concomitantly, we neglect the convection induced by a thermal gradient (as in Bénard's

thermo-convection). This is justified as there are very few experiments on natural convection involving nanoparticles and the results are not conclusive [25]. The effect of electric surface charge is to modify the structure of the solid particles; however, the study of its consequence is outside the scope of this work as well as the role of surfactants which is of more importance in the methods of preparation of the nanofluids.

The process of homogenization of the heterogeneous medium, formed by the nanoparticles and the host fluid, is based on the EMA formalism. The latter finds its origin in a work by Maxwell [7] (in the framework of electric conductivity) and has been revisited later on by Nan et al [8] (in a different context). These authors propose a methodology for determining the effective heat conductivity of nanocomposites taking into account the interfacial thermal resistance, size, shape and orientation of the particles. Their approach has been applied to a large variety of geometries and is based on a multiple-scattering technique [8]. The EMA equation for the effective thermal conductivity coefficient, k^{eff} as derived by Nan et al. is given by

$$k^{eff} = k_f \frac{2k_f + (1+2\alpha)k_p + 2\varphi\left[(1-\alpha)k_p - k_f\right]}{2k_f + (1+2\alpha)k_p - \varphi\left[(1-\alpha)k_p - k_f\right]}. \tag{1}$$

In this expression, k_f and k_p designate the thermal conductivities of the fluid and the suspended particles respectively, φ is the volume fraction of the particles and α is a dimensionless parameter describing the particle-fluid interaction expressed by

$$\alpha = Rk_f/r_p. \tag{2}$$

with r_p the radius of the nanoparticle, and R the thermal boundary resistance coefficient whose magnitude is 0.77*10^-8, 1.2*10^-8 and 0.92 *10^-8 Km²/W for water, ethylene glycol and the 50/50

w% water/ethylene-glycol mixture, respectively [37]. The values of k_f are obtained from the literature [38], while k_p is derived hereafter on the bases of EIT [12, 34], leading to

$$k_p = k_p^0 \, f(Kn), \qquad (3)$$

with $f(Kn)$ the correcting factor allowing for the size dependence of the nanoparticles, the quantity k_p^0 is the value of the thermal conductivity for the bulk material of which the particle is composed of and is given by the classical relation

$$k_p^0 = \frac{1}{3}(C_p v_p \Lambda_p) \qquad (4)$$

wherein C_p, v_p and Λ_p stand for the specific heat capacity, the group velocity and the mean free path of phonons respectively. The correction factor $f(Kn)$, expresses the dependence with respect to the particle's size through Kn, the Knudsen number, defined as the ratio of the mean free path Λ_p of the phonons inside the particle and the radius r_p of the particle:

$$Kn = \Lambda_p / r_p. \qquad (5)$$

The function $f(Kn)$ in (3) is determined by referring to EIT. According to EIT, the space V of state variables describing a rigid heat conductor is constituted by the internal energy, the only relevant conserved variable, e (or the temperature T) and the non-conserved heat flux vector q so that $V = (e, q)$. Nanomaterials require the introduction of higher order heat fluxes, like $Q^{(2)}$ (a tensor of order two), the flux of q, $Q^{(3)}$ (a tensor of order three), the flux of $Q^{(2)}$ and so on. An important problem is to derive their time evolution equations. This task is easily achieved

by determining the expression of the rate of entropy production. The latter is obtained by starting from the expression of the entropy function $s(V)$, assumed to depend on the whole set V of variables. Here $s = s(e, q, Q^{(2)}, ..., Q^{(N)})$ or in terms of time derivatives,

$$d_t s(e, q) = \frac{\partial s}{\partial e} d_t e + \frac{\partial s}{\partial q} \cdot d_t q + \sum_{n=2}^{N} \frac{\partial s}{\partial Q^{(n)}} \otimes d_t Q^{(n)}, \tag{6}$$

wherein e and s are measured per unit volume, a dot stands for the scalar product, the symbol $\otimes$ for the inner product of the corresponding tensors and d_t for the material time derivative. Expression (6) is referred to as the generalized Gibbs equation. It is assumed that s is a concave function of the variables to guarantee stability of the equilibrium state. Moreover, it obeys a general balance equation of the form

$$d_t s = -\nabla \cdot J^s + \sigma^s \qquad (\sigma^s \geq 0), \tag{7}$$

whose rate of production per unit volume σ^s (in short, the entropy production) is positive definite to satisfy the second principle of thermodynamics, J^s is the entropy flux vector. Now, define the non-equilibrium temperature by $\partial s / \partial e = T^{-1}(e)$, wherein the fluxes have been neglected [39], and select the constitutive equations for $\partial s / \partial q$, $\partial s / \partial Q^{(n)}$ as given by $\partial s / \partial q = -\alpha_1(T) q$ and $\partial s / \partial Q^{(n)} = -\alpha_n(T) Q^{(n)}$, respectively. $\alpha_n(T)$ $(n = 2, ... N)$ are positive definite coefficients to meet the property that s is maximum at equilibrium. They depend generally on the temperature, the minus sign in front of $\alpha_n(T)$ having been introduced for convenience. Under these conditions, expression (6) can be written as

$$d_t s(e, q, Q^{(2)}, ..., Q^{(N)}) = T^{-1} d_t e - \alpha_1 q \cdot d_t q - \alpha_2 Q^{(2)} \otimes d_t Q^{(2)} - \cdots - \alpha_N Q^{(N)} \otimes d_t Q^{(N)}.$$

$$\tag{8}$$

The next step is the formulation of the entropy flux J^s, which is not simply given by the classical expression $T^{-1}q$ like in classical irreversible thermodynamics [39], but in EIT, it also depends generally on the higher order fluxes. According to the theory of representation of isotropic tensors [40] a general expression of the vector J^s depending on the variables q, $Q^{(2)}$, ...$Q^{(2)}$ is

$$J^s = T^{-1}q + \beta_1 Q^{(2)} \cdot q + \cdots + \beta_{N-1} Q^{(N)} \otimes Q^{(N-1)}, \tag{9}$$

with β_n designating material quantities, whose physical meaning will be specified in the forthcoming. Substituting (8) and (9) in (7), and eliminating $d_t e$ via the energy conservation law ($d_t e = -\nabla \cdot q$) leads to

$$\sigma^s = -\left(-\nabla T^{-1} + \alpha_1 d_t q - \beta_1 \nabla \cdot Q^{(2)}\right) \cdot q - \sum_{n=2}^{N} Q^{(n)} \otimes \left(\alpha_n d_t Q^{(n)} - \beta_n \nabla \cdot Q^{(n+1)} - \beta_{n-1}\nabla Q^{(n-1)}\right) \geq 0, \tag{10}$$

where, for $n = 2$, $Q^{(1)}$ is to be identified as q. The expression for σ^s is a bilinear relationship in the flux q and the subsequent higher order of fluxes $Q^{(n)}$. The terms between the parentheses are usually called the thermodynamic force X. In order to guarantee the positiveness of the entropy production σ^s, the simplest way is to assume a linear flux-force relation of the form $X^{(n)} = \mu_n Q^{(n)}$ ($\mu_n > 0$ & $n = 1,2,3, ...$), where μ_n are phenomenological coefficients. In doing so, we obtain the set

$$\nabla T^{-1} - \alpha_1 \partial_t q + \beta_1 \nabla \cdot Q^{(2)} = \mu_1 q, \tag{11}$$

$$\beta_{n-1}\nabla \boldsymbol{Q}^{(n-1)} - \alpha_n \partial_t \boldsymbol{Q}^{(n)} + \beta_n \nabla \cdot \boldsymbol{Q}^{(n+1)} = \mu_n \boldsymbol{Q}^{(n)}, (n = 2,3, \dots, N), \tag{12}$$

which is compatible with positive entropy production at the condition that $\mu_n > 0$. In (11) and (12), we have replaced the material by the partial time derivative as the heat conductor is assumed at rest, while α_n, β_n and μ_n are phenomenological coefficients related to the relaxation times, correlation lengths and transport coefficients, respectively. For instance, by setting in Equation (11), $\alpha_1 = \tau/kT^2$ and $\mu_1 = 1/kT^2$, with τ designating the relaxation time of the heat flux, expression (11) reduces to the well-known law of Cattaneo when the term $\nabla \cdot \boldsymbol{Q}^{(2)}$ is omitted. The other coefficients α_n and μ_n ($n = 2, \dots, N$) associated to the higher order fluxes, can be given a similar meaning. Consider now an infinite number of flux variables ($N \to \infty$) and apply the spatial Fourier transform $\hat{\boldsymbol{q}}(\boldsymbol{k}, t) = \int_{-\infty}^{+\infty} \boldsymbol{q}(\boldsymbol{r}, t) e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \, d\boldsymbol{r}$ to Eqs. (11) and (12), with $\hat{\boldsymbol{q}}$ the Fourier transform of $\boldsymbol{q}$, $\boldsymbol{r}$ the spatial variable, t the time and $\boldsymbol{k}$ the wavenumber vector. This procedure yields the following time-evolution equation for the heat flux

$$\bar{\tau}(\boldsymbol{k})\partial_t \hat{\boldsymbol{q}}(\boldsymbol{k}, t) + \hat{\boldsymbol{q}}(\boldsymbol{k}, t) = -ikk_p(\boldsymbol{k})\hat{T}(\boldsymbol{k}, t) \tag{13}$$

where $\bar{\tau}(\boldsymbol{k}) = \alpha_1/\mu_1$ designates a renormalized relaxation time depending generally on $\boldsymbol{k}$, while the thermal conductivity $k_p(\boldsymbol{k})$ is given by the continued-fraction

$$k_p(\boldsymbol{k}) = \cfrac{k_p^0}{1 + \cfrac{k^2 l_1^2}{1 + \cfrac{k^2 l_2^2}{1 + \cfrac{k^2 l_3^2}{1 + \cdots}}}}, \tag{14}$$

with k_p^0 the classical bulk thermal conductivity, given by Eq. (4), independent of the dimension of the system, l_n is the correlation length of order n defined by $l_n^2 = \beta_n^2/(\mu_n \mu_{n+1})$. Here, it is

assumed that the relaxation times τ_n ($n > 1$) corresponding to higher order fluxes are negligible with respect to τ_1, which is a hypothesis generally admitted in kinetic theories. In the present problem, there is only one characteristic dimension (the nanoparticle radius), so that it is natural to select $k \equiv 2\pi/r_p$. The correlation lengths are selected as [30,41,42]

$$l_n^2 = a_{n+1}l^2, \tag{15}$$

with $a_n = n^2/(4n^2 - 1)$ and l identified as a reference length independently of the order of approximation. With these results in mind, it was shown (e.g. [30,41]) that within the asymptotic limit $n \to \infty$ [43], the continued fraction (14) may be given the form

$$k_p = \frac{3k_p^0}{4\pi^2 Kn^2}\left[\frac{2\pi Kn}{arctan(2\pi Kn)} - 1\right]. \tag{16}$$

Substitution of relation (16) in (1) closes the problem of determining the effective thermal conductivity of the nanofluid.

3. Influence of several heat transfer mechanisms

In this section, the influence of several heat transfer mechanisms, with the aim to determine their relative importance, is investigated. The effects considered in the forthcoming are successively those caused by the presence of a liquid layer around the nanoparticles (liquid-layering), particles agglomeration and Brownian motion of particles.

3.1. Liquid layering

Because of the strong interatomic forces at the interface particles-fluid, some of the fluid molecules will attach themselves to the surface of the nanoparticle, forming an interfacial layer

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of thickness δ with a higher density than the fluid and having the property approaching that of the solid phase of the fluid [25]. As this "solid" surrounding layer has its own thermal conductivity, it is expected that it will influence the heat transfer mechanism. A possible way to take into account the liquid-layer effect is to modify relation (1), so that we are led to [13-16]

$$k_{ll}^{eff} = k_f \frac{2k_f + (1+2\alpha_l)k_{pl} + 2\varphi(1+\beta)^3 \left[(1-\alpha_l)k_{pl} - k_f\right]}{2k_f + (1+2\alpha_l)k_{pl} - \varphi(1+\beta)^3 \left[(1-\alpha_l)k_{pl} - k_f\right]}, \qquad (17)$$

where index *"ll"* stands for "liquid layer" and k_{pl} for the thermal conductivity of the nanoparticle with the surrounding layer. The presence of the liquid layer of thickness δ will modify the radius of the particle from r_p to $r_p + \delta$ and the volume fraction from φ to $\varphi(1+\beta)^3$ with $\beta = \frac{\delta}{r_p}$, the ratio of the liquid layer thickness and the nanoparticle radius [13] ($\beta \to 0$ means that the liquid-layer effect is not taken into account). Finally, in analogy with expression (1), the equivalent thermal conductivity of the heterogeneous system formed by the nanoparticle and the liquid layer is given by:

$$k_{pl} = k_p \frac{\gamma \left(2(1-\gamma) + (1+\beta)^3(1+2\gamma)\right)}{(\gamma-1) + (1+\beta)^3(1+2\gamma)}, \qquad (18)$$

where $\gamma = \frac{k_l}{k_p}$, is the ratio of the thermal conductivities of the liquid layer (k_l) and the nanoparticle k_p (given by Eq. (16)). It is expected that the solid-like liquid layer has a thermal conductivity intermediate between that of the bulk liquid and that of the nanoparticle. Xie et al. [13] propose

$$k_l = \frac{k_f M^2}{(M-\beta)\ln(1+M) + \beta M}, \qquad (19)$$

with $M = (k_p/k_f)(1 + \beta) - 1$. It remains to determine the liquid layer thickness δ around the nanoparticle. Based on the electron density profile at the interface, Hashimoto et al. [44] derived the interfacial layer thickness at the surface of a spherical micro-domain. Later, Li et al. [45] introduced the same model for determining the interfacial layer thickness of a pseudo solid–liquid system. In both works, $\delta = \sqrt{2\pi}\sigma$, where σ is a characteristic length related to the diffuseness of the interfacial boundary, with a typical value that falls in the range 0.4-0.6 nm, from which follows that δ is of the order of 1-1.5 nm. In addition, experimental results [46] and molecular dynamics simulations [47] showed that the typical interfacial layer thickness between the solid (nanoparticles) and liquid phase is of the order of a few atomic distances, namely, 1-2 nm. Murshed et al. [48] also reported that the variation of the interfacial layer thickness (they considered 1-3 nm) does not significantly affect the thermal conductivity enhancement. Accordingly, we expect that there is not much difference between 1 and 1.5 nm for the interfacial layer (this has been also confirmed by a posteriori calculations). For the sake of completeness, we have studied the impact of choosing a higher value, say δ = 3 nm (the maximum value being generally considered [48]). As commented in Section 4.3, a modification of the value of δ has little influence so that it is reasonable to use δ = 1 nm in the calculations as widely accepted in the literature [44, 45, 48].

3.2. Agglomeration of particles

We now allow some of the particles to form clusters supposed to be uniformly dispersed within the fluid with their distributions independent of the space coordinates. To account for the agglomeration of nanoparticles [49-52], we will change the radius r_p of the particles into $r_{p,a}$ (radius of the agglomerate) in the expressions of α_a and β_a, which reads respectively, $\alpha_a = \frac{Rk_f}{r_{p,a}+\delta}$ and $\beta_a = \frac{\delta}{r_{p,a}}$. In these expressions, we have introduced the thickness δ of the liquid layer

because agglomeration and liquid-layering are linked to one another, indeed liquid layers may also be found around agglomerates. The quantity $\varphi_a = \varphi \left(\frac{r_{p,a}}{r_p} \right)^{3-D}$ is the volume fraction of the agglomerates, with D the fractal index, whose typical value lies between 1.6 and 2.5 for aggregates of spherical nanoparticles [51]. The value for D is often taken as 1.8 and since the thermal conductivity appears to be rather insensitive to the value of D [50-52], we will here work with $D = 1.8$. This leads finally to the following expression for the effective thermal conductivity $k_{ll,a}^{eff}$ taking into account the agglomeration and the liquid-layer effects:

$$k_{ll,a}^{eff} = k_f \frac{2k_f+(1+2\alpha_a)k_{a,l}+2\varphi_a(1+\beta_a)^3\left[(1-\alpha_a)k_{a,l}-k_f\right]}{2k_f+(1+2\alpha_a)k_{a,l}-\varphi_a(1+\beta_a)^3\left[(1-\alpha_a)k_{a,l}-k_f\right]}. \qquad (20)$$

In Eq. (20), we have introduced the quantity $k_{a,l}$, which is the thermal conductivity of an agglomerate formed by the cluster of particles surrounded by a liquid layer. We use for $k_{a,l}$ the expression established by Hui et al. [53] and adapt it by introducing the liquid-layer effect in the same way as done in the previous subsection, resulting into

$$k_{a,l} = \frac{1}{4}\left[3\varphi_s(k_p - k_f) + (2k_f - k_p) + \sqrt{8k_f k_p + \left(3\varphi_s(k_f - k_p) + (k_p - 2k_f)\right)^2} \right], \quad (21)$$

where $\varphi_s = \frac{\varphi}{\varphi_a}$ is the ratio of the volumes occupied by the particles and the aggregates. By letting δ tend to zero, one obtains the effective thermal conductivity accounting for agglomeration only, as $k_{ll,a}^{eff}|_{\delta \to 0} \equiv k_a^{eff}$. With $k_{ll,a}^{eff}|_{r_{p,a} \to r_p} \equiv k_{ll}^{eff}$, one finds back the expression of the effective thermal conductivity accounting only for the liquid layer effect. Finally, we recover Eq. (1) by noticing that $k_{ll,a}^{eff}|_{r_{p,a} \to r_p \ \& \ \delta \to 0} \equiv k^{eff}$.

3.3. Brownian motion

In this subsection, we consider another mechanism, namely the Brownian motion of nanoparticles, this effect finds its origin in the stochastic bombardment of the liquid host molecules and results in micro convections at the nano scale and whence, enhancement of thermal interactions between the nanoparticles and the ambient fluid [21-23, 37]. The contribution to the effective heat conductivity may be expressed as an additional term k_{Br} given by Jang and Choi [23]:

$$k_{Br} = \frac{h \delta_H \varphi}{Pr_f},$$
(22)

where Pr_f stands for the Prandtl number of the base fluid

$$Pr_f = \frac{\mu_f c_f}{k_f}$$
(23)

with μ_f and c_f being the kinematic viscosity and the specific heat capacity of the fluid, respectively, while δ_H is the so-called hydrodynamic boundary layer thickness. Several options have been proposed for δ_H, for instance, Jang and Choi [23] argued that δ_H is of the order of three times the diameter of the fluid molecules. In a later publication [38], the same authors assume that it is comparable to the size of the fluid molecules. Nonetheless, Yu et al. [46] and Prasher et al. [54] take δ_H equal to three times the molecule diameters as well. We adopt here the same position, meaning that $\delta_H \equiv 0.9$ nm for water, $\delta_H \equiv 1.2$ nm for ethylene glycol and $\delta_H \equiv 1$ nm obtained by taking the molar average value for a 50/50 w% water/ethylene-glycol mixture.

Furthermore, the factor h in relation (22) is an overall heat transfer coefficient at the surface of the particles given by Jang and Choi [23]

$$h = \frac{Nu_f \, k_f}{2(r_p + \delta)},$$
(24)

with Nu_f designating the Nusselt number, which for a flow past a sphere is [6, 23, 38]

$$Nu_f = 2 + \frac{1}{2} Re_f Pr_f,$$
(25)

Re_f is the Reynolds number, given by

$$Re_f = \frac{k_B T \rho_f}{3\pi \mu_f^2 \delta_H},$$
(26)

where ρ_f is the base fluid density, k_B the Boltzmann constant and T the temperature.

When liquid layering and agglomeration are negligible, the effective thermal conductivity k_{Br}^{eff} of the nanofluid may be written as

$$k_{Br}^{eff} = k^{eff} + k_{Br},$$
(27)

with k^{eff} expressed by relation (1).

When all the mechanisms considered in this work are taken into account, namely, liquid-layering, agglomeration and Brownian motion, the total effective thermal conductivity (k_{tot}^{eff}) writes as

$$k_{tot}^{eff} = k_{ll,a}^{eff} + k_{Br},$$ (28)

with $k_{ll,a}^{eff}$ given by (11). Note that k_{tot}^{eff} is not just simply the sum of the various mechanisms, taken individually, but rather includes all the interacting couplings.

4. Numerical results and discussion

4.1. Thermal conductivities of alumina-water, alumina-ethylene glycol and alumina-50/50 w% water/ethylene-glycol mixture nanofluids

In this section are discussed the various contributions to the effective thermal conductivity k_{tot}^{eff} as a function of the volume fraction of nanoparticles and their size in the following situations, respectively:

- k^{eff}: without the considered heat transfer mechanisms (Eq. (1)),

- k_{ll}^{eff}: liquid-layering alone (Eq. (17)),

- k_a^{eff}: agglomeration alone (Eq. (20) wherein $\delta = 0$),

- k_{Br}^{eff}: Brownian motion alone (Eq. (27)),

- k_{tot}^{eff}: incorporating all the considered heat transfer mechanisms (Eq. (28)).

Note that the maximum volume fraction value may not be extended to $\varphi = 1$ but is limited by the maximum packing of spheres, namely $\varphi_{max} = \pi/\sqrt{18}$. The calculations are performed for suspensions of alumina spherical nanoparticles in water, ethylene glycol and a 50/50 w% water/ethylene-glycol mixture, respectively. The theory is of course by no means limited to these fluids which have been selected because they allow a direct comparison with

experimental data [19, 56-61]. The material properties of alumina used for the calculations are given in Table 1 and refer to the room temperature (taken here to be 300 K).

Table 1. Room temperature material properties for alumina (Al_2O_3) particles [55].

Material	Heat capacity [MJ/(m^3K)]	Group velocity [m/s]	Mean free path [nm]
Al_2O_3	3.04	7009	5.08

The thermal conductivities k_f of the base fluids are 0.613, 0.252 and 0.4 Wm^{-1}K^{-1} for water, ethylene glycol and the 50/50 w% water/ethylene-glycol mixture, respectively [38, 62]. Water and ethylene glycol are common heat transfer fluids, but they present the characteristic to have limited heat transfer capabilities [56]. This explains the interest in enhancing their heat transfer properties by adding nanoparticles. The results are presented in Figs. 1-3, with the thickness of the liquid boundary layer given by $\delta = 1$ nm. The experimental values are taken from [19, 56-61].
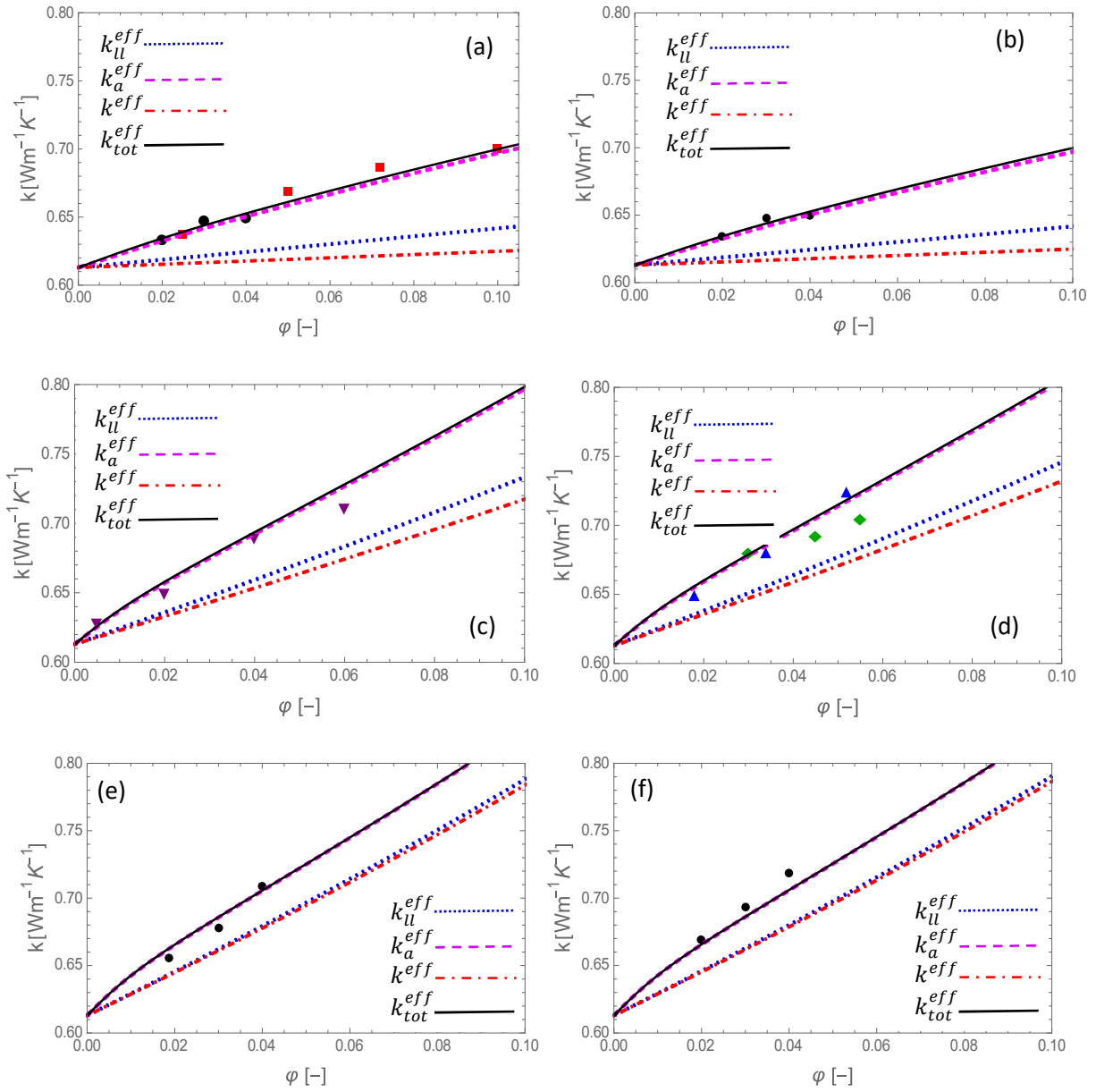
Fig. 1 Effective thermal conductivities (k_{ll}^{eff}, k_a^{eff}, k^{eff} and k_{tot}^{eff}) of alumina-water nanofluids as a function of the volume fraction for different nanoparticle radii (r_p): (a) 6 nm, (b) 8 nm, (c) 23.5 nm, (d) 30 nm, (e) 122.5 nm and (f) 141 nm. Experimental values are drawn from [19] ■, [56] ◆, [57] ▲, [59] ● and [60] ▼.
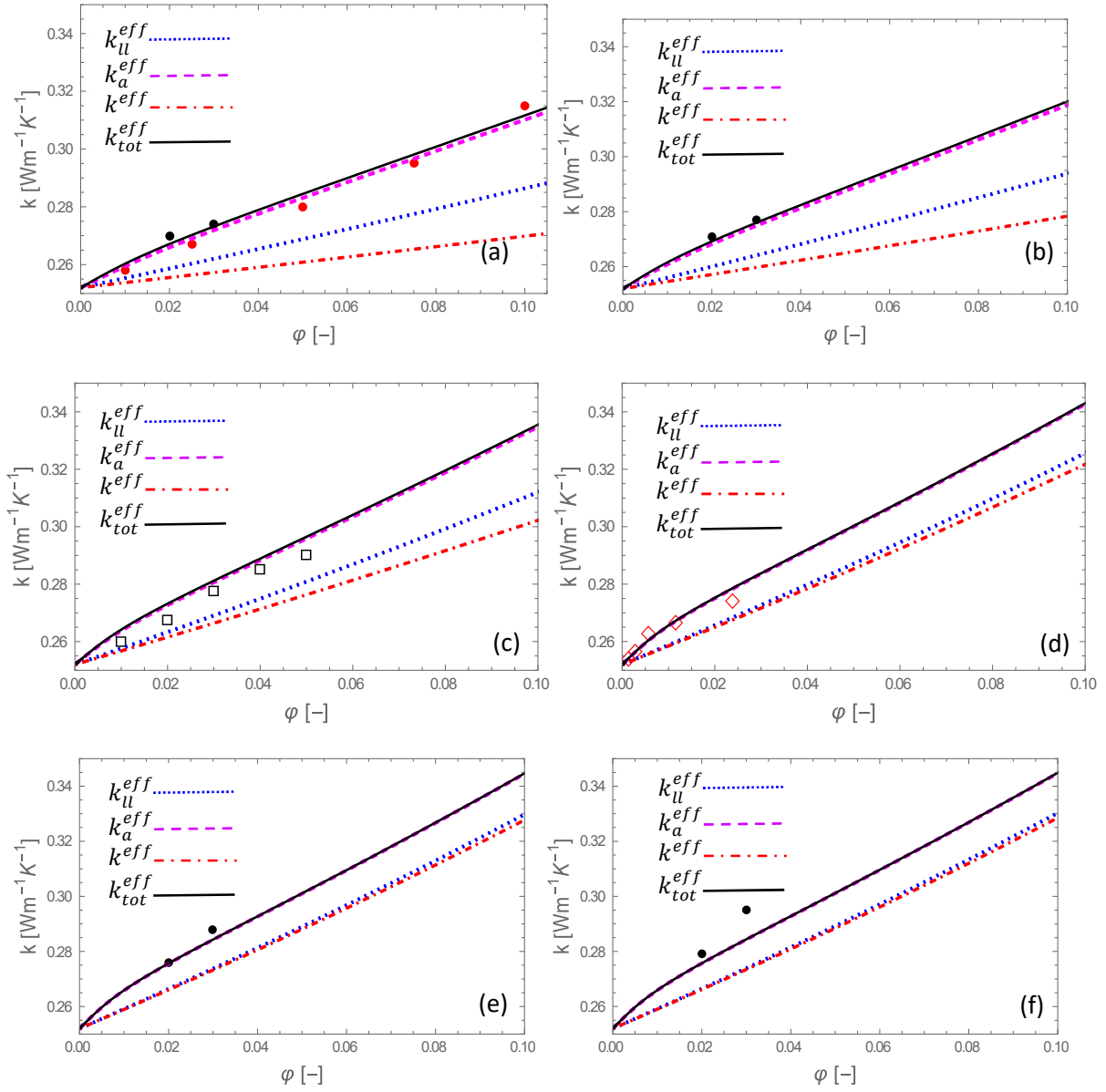
Fig. 2 The same as in Fig. 1 for alumina-ethylene glycol nanofluids with nanoparticle radii (r_p): (a) 6 nm, (b) 8 nm, (c) 19 nm, (d) nm, (e) 122.5 nm and (f) 141 nm. Experimental values are drawn from [19] ●, [58] ◊, [59] ● and [61] □.
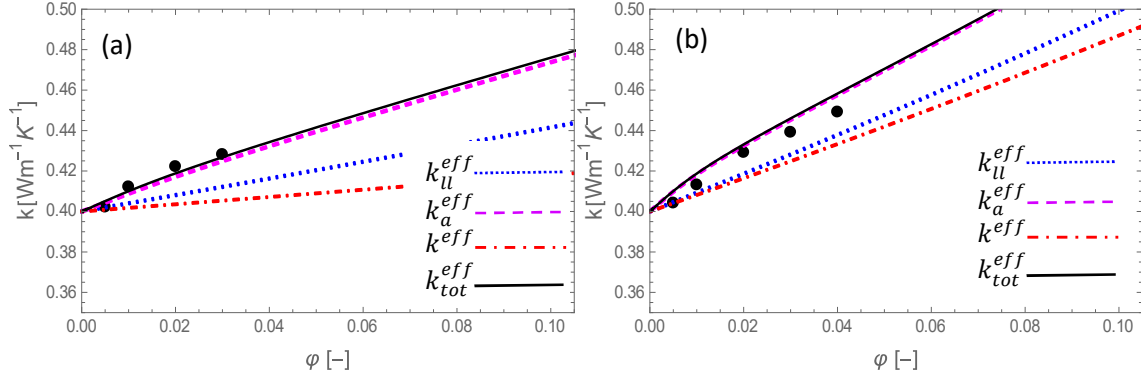
Fig. 3 The same as in Fig. 1 for alumina-50/50 w% water/ethylene-glycol nanofluids with nanoparticle radii (r_p): (a) 5 nm, (b) 25 nm. Experimental values ● are drawn from [62].

The general trend is that the thermal conductivity is enhanced by more than 20% for an increase of 10% of the volume fraction. Experimental data are not available for any particle size and volume fraction and, therefore, the theoretical predictions are compared with several different experimental sources. A satisfactory agreement with the available experimental data is observed. The full model k_{tot}^{eff} fits reasonably well the experiments except at one point for ethylene glycol, namely $r_p = 141$ nm, $\varphi = 0.035$ (Fig. 2(f)). This may be due to the uncertainty about the degree of agglomeration whose value is not experimentally univocally determined [18]. Nevertheless, it can be said that k_{tot}^{eff} is of the same order of magnitude as the experimental data. It is interesting to see to which extent the results, predicted by considering only one single heat transfer mechanism, namely either k_{ll}^{eff}, k_a^{eff} or k_{Br}^{eff}, may be different from k_{tot}^{eff}. Our calculations have shown that the difference between k_{Br}^{eff} and k^{eff}, expressed by equation (1), is too small to be reproducible on the graphs, so that we feel legitimate to take $k_{Br}^{eff} \approx k^{eff}$ and to represent only k^{eff}. The validity of this assumption is discussed in the next subsection. We observe that k_a^{eff} is closer to k_{tot}^{eff} than k_{ll}^{eff}, whatever the sizes of the nanoparticle. As the nanoparticle radius increases, the difference $k_a^{eff} - k^{eff}$ increases, while $k_{ll}^{eff} - k^{eff}$ decreases. One important feature is that different particle dimensions lead to different outcomes.

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The crucial role played by the particle size justifies that it be further investigated. Beforehand, let us comment about the controversial role of Brownian motion on heat transfer in nanofluids.

4.2. Note on the Brownian motion

The behavior of the effective thermal conductivity of Al$_2$O$_3$-ethylene glycol and Al$_2$O$_3$-water nanofluids versus the particle size is analyzed. Two different volume fractions (1% and 5%) are considered.

In Fig. 4 are compared the values of the effective thermal conductivity (in absence of agglomeration and liquid layering effects) with and without Brownian motion for alumina particles dispersed in water and ethylene-glycol, respectively.
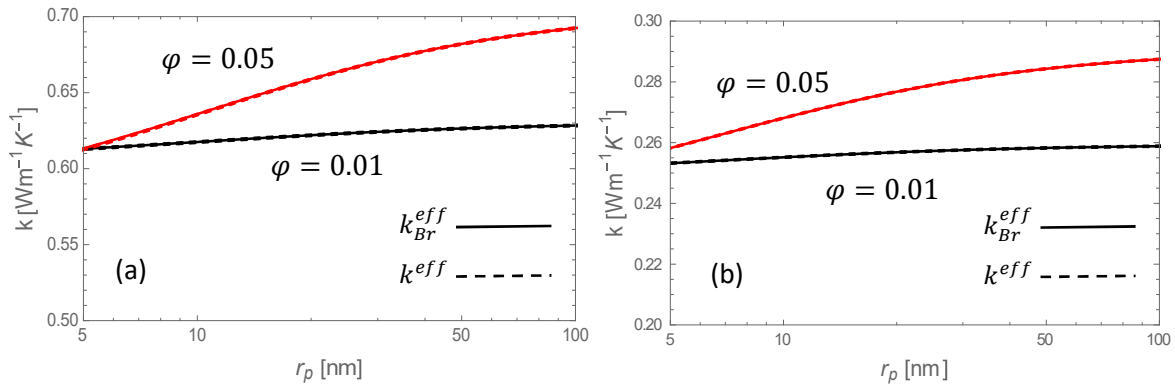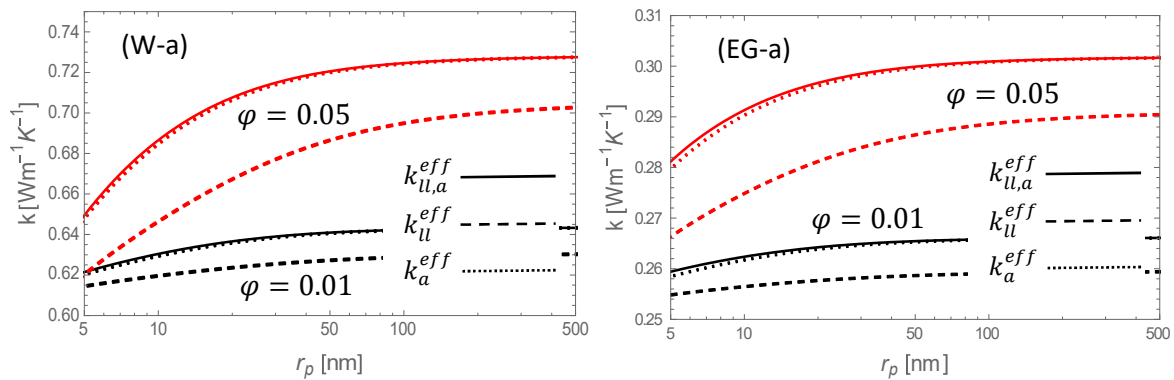

Fig. 4 Effective thermal conductivity k_{Br}^{eff}, compared to k^{eff} versus the nanoparticle radius at volume fractions of 1% (lower curves) and 5% (upper curves), for alumina nanoparticles in (a) water (solid lines) and (b) ethylene glycol (dashed lines).

It appears that Brownian motion (k_{Br}^{eff}) does not significantly modify (less than 1 %) the basic thermal conductivity (k^{eff}). It may therefore be concluded from our analysis that the

Brownian motion is of no great influence, at least for the considered nanofluids. The influence of Brownian motion on heat transfer in nanofluids was investigated in several papers [21-23, 63-70] but most of these studies disagree about its importance. For instance, on the basis of the kinetic theory, Jang and Choi [23] claimed that the Brownian motion is one of the key mechanisms in the enhancement of the thermal conductivity. However, for others, like Gupta and Kumar [65], Nie et al. [67] and Evans et al. [70], the Brownian motion does not play a significant role in agreement with the results of the present work. Nonetheless, it is true that for nanofluids with a low viscous base fluid or aerosols, the Brownian effect may become relevant.

4.3. Thermal conductivity as a function of the particle size

The above considerations allow us to omit the Brownian motion and to focus on the agglomeration and liquid layering effects. In Fig. 5 are shown as a function of the particle radius, the separate influences of agglomeration (k_a^{eff}), nano-layering (k_{ll}^{eff}) and the coupling agglomeration-nano-layering ($k_{ll,a}^{eff}$) for water and ethylene glycol; two values of the particles volume fraction and two values of the liquid boundary layer thickness are considered.
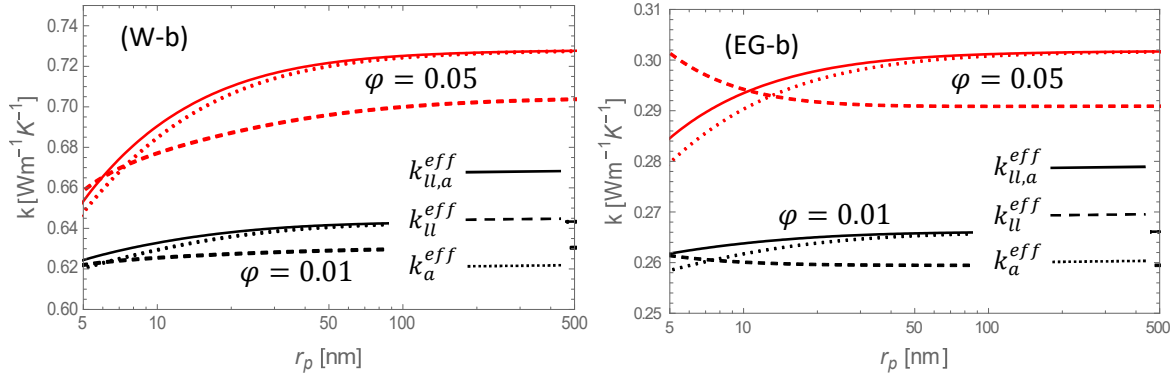
Fig. 5 Effective thermal conductivity $k_{ll,a}^{eff}$ (solid lines) compared to k_{ll}^{eff} (dashed lines) and k_a^{eff} (dotted lines) versus the nanoparticle radius at volume fractions of 1% (lower curves) and 5% (upper curves), for (a) $\delta = 1$ nm and (b) $\delta = 3$ nm. The nanofluids consist of alumina nanoparticles in water (W) and ethylene glycol (EG).

The general tendency is the increase of the thermal conductivity with, from one side, the volume fraction, and, from the other side, with the particle size. The presence of an asymptotic value is confirmed for $r_p > 100$ nm. This is understandable because for relatively large particles with respect to the mean free paths, the size will no longer influence the value of the thermal conductivity. Indeed, at large sizes the Knudsen number becomes very small ($k_p \rightarrow k_p^0$ in Eq. (16)), indicating that heat transport is no longer of ballistic but rather of diffusive nature, governed by Fourier's law. The results in Fig. 5 show that the behavior of the thermal conductivity, especially at $r_p \approx O(1\text{-}10)$ nm, is strongly dependent on the thickness of the interfacial layer and the rate of agglomeration. For particles in the range of molecular scale, it is observed experimentally [59] and computationally [71] that the thermal conductivity increases with increasing size, as seen in Figs. 5 (W-a) and 5 (EG-a). This behavior was confirmed by several experimental works [19, 61, 72]. However, it was mentioned by Keblinski et al. [2] that the thermal conductivity may rather decrease for increasing particle sizes in presence of highly conducting liquid layers around the nanoparticles, such a conclusion is

supported by our developments (in absence of agglomeration) as shown by the dashed curves of Fig. 5 (EG-b). At larger particle dimensions ($r_p \geq 10$ nm), the thickness δ of the interfacial liquid hardly influences the value of the effective thermal conductivity, from which can be deduced that, at relatively large sizes, agglomeration appears to be the dominant effect, as confirmed by experiments [2].

5. Complementary comments

To shed a different light on the above developments, we have calculated the so-called enhancement factor EF (in %), defined as the ratio of the thermal conductivity enhancement, $k_i^{eff} - k^{eff}$ (with the subscript i designating the mechanism under study: either Brownian motion, liquid layering or particles agglomeration) to the overall enhancement defined as $\left(k_{ll}^{eff} - k^{eff}\right) + \left(k_a^{eff} - k^{eff}\right) + \left(k_{Br}^{eff} - k^{eff}\right)$.
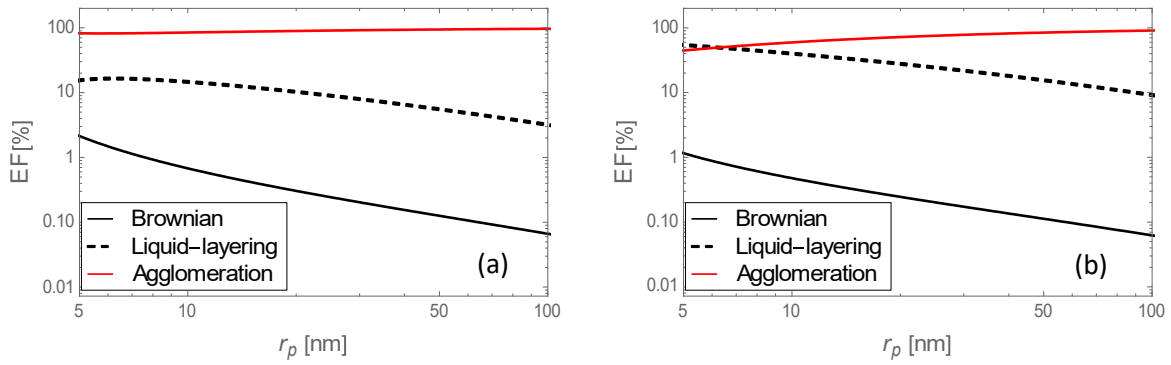

Fig. 6 Enhancement factor EF for alumina nanoparticles in water calculated for the different heat transfer mechanisms as a function of the nanoparticle radius for (a) $\delta = 1$ nm and (b) $\delta = 3$ nm. The volume fraction is 1%.
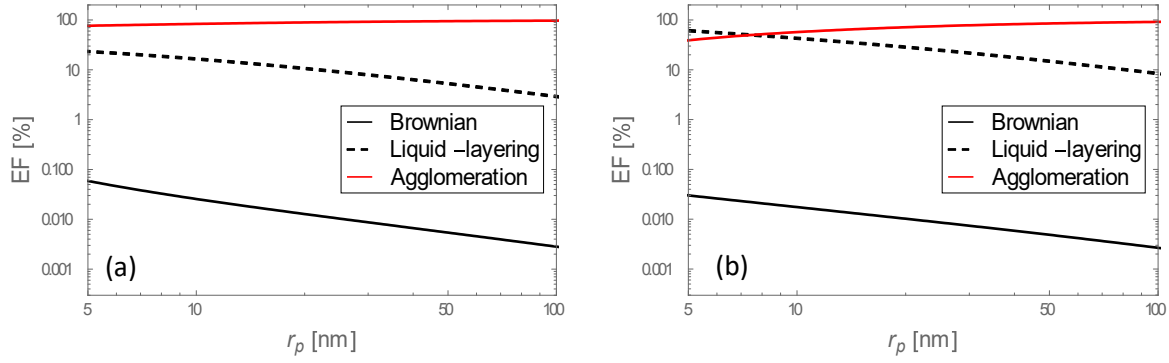
Fig. 7 The same as in Fig. 6 for alumina nanoparticles in ethylene glycol.

The results of the previous figures are confirmed for alumina in water (Fig. 6) and ethylene glycol (Fig. 7). It is observed that the role of Brownian motion is minute and that both liquid-layering and agglomeration are the leading heat transfer mechanisms, depending on specific conditions: the thickness of the liquid-layering and the nano-particle size. Similar conclusions can be drawn for the 50/50 w% water/ethylene-glycol mixture.

6. Conclusions

The aim of this paper is to examine the relative importance of various mechanisms responsible for the enhancement of the effective thermal conductivity of nanofluids. The novelty of the present approach is that the several mechanisms are not studied separately, as in most previous papers, but are examined all together. An original model is proposed, mixing the effective medium approach (EMA) and Extended Irreversible Thermodynamics (EIT), resulting into fully analytical expressions of the effective thermal conductivity (see formulae (17), (20), and (28)).

At small-length scales, heat transport in the particles is no longer governed by diffusive collisions of the heat carriers but rather by ballistic conduction. As a consequence, Fourier's law is no longer valid and must be replaced by more sophisticated relations as accounted for by expression (16) of the thermal conductivity of the nanoparticles.

A huge variety of mechanisms are able to influence the heat conductivity of nanofluids and it is illusory to include all of them into one single model. In the present analysis, we have focused on some specific mechanisms which in our opinion play a relevant role. Accordingly, we have successively examined the influence of formation of "solid-like" liquid layers at the liquid-particle interface, agglomeration of particles and Brownian motion. Other factors, like porosity, the presence of electric charges and/or surfactants are not investigated and the modelling is restricted to spherical particles of the same dimension.

Our main contributions are to show

1. that the particle size and the thickness of the liquid boundary layer are the relevant parameters in determining which mechanism is the main responsible for heat transfer.

2. that agglomeration of particles and nano-layer effects are dominant

3. the role of Brownian effect in heat transfer, a controversial subject, is of importance for nanoparticles with dimensions of the order of those of molecules ($r_p <$ O(1) nm).

Summing up, it results from our study that clustering of particles turns out to have the upper hand with respect to the presence of a liquid nano-layer for large particle sizes $r_p >$ O(10) nm. This is quite understandable, since the agglomeration radius becomes larger as the particle size increases, whilst for large particles the nanolayer thickness becomes negligible with respect to the agglomeration radius. In the intermediate region (1 nm $< r_p <$ 10 nm), the nano-layer effect may be of more importance depending on the thickness of the layer.

Comparison with experimental data have concerned three particular situations, namely alumina particles dispersed in water, ethylene glycol and a 50/50 w% water/ethylene-glycol mixture, respectively, for which experimental data were available. It is our meaning that our approach, which is based on the recent developments of non-equilibrium thermodynamics, is sufficiently general to be applicable to a wider class of nanofluids.

In contrast with most papers wherein the various heat transfer mechanisms are treated separately, the general overview proposed in this work allows to compare between their relative importance, to distinguish which of them is dominating under given circumstances, and to conciliate the contradictory results in the literature. Our main contribution is to provide a coherent modelling of a series of mechanisms governing heat transfer in nanofluids in agreement with experimental observations.

Acknowledgments

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