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Scaling On Transport Properties of Nanofluids for Heat Transfer Applications

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Abstract **-** In the last century, Andrade proposed a theory of the viscosity of liquids based on a molecular approach and, similarly, Osida established a model for the thermal conductivity of liquids. Based on these studies, Mohanty developed an equation that involves the transport properties of liquids, recognising the need of further contributions to refine his proposal. In this work, a new relationship is proposed taking into account the particular case of the nanofluids as complex multivariable thermodynamic systems. Thus, this novel empirical equation is described in terms of the balance between the thermal conductivity enhancement and the penalty of the viscosity increase. The reliability of this proposed relationship was checked by experimental data available in the nanofluids literature for magnesium oxide within *n*-tetradecane, silver within poly(ethylene glycol), titanium oxide within water, and aluminium oxide within (1-ethyl-3-methylimidazolium methanesulfonate + water).

Keywords**:** nanofluids; transport properties; thermal conductivity; viscosity; heat transfer

1. Introduction

Several attempts in the early twentieth century to extend the kinetic theory of gases to liquids [1−3] failed to produce an unquestionable agreement with experimental evidence [4]. Andrade [5] introduced a theory of liquid viscosity based on simple classical approaches without considering any quantum explanation that would not cause significant changes in the results [6]. He thought that a theory of liquids should be addressed from the standpoint of the solid state rather than the kinetic theory of gases [5], because the distances between molecules are much more solid-like and, as a result, intermolecular forces are similar. From a molecular point of view, the major difference between a liquid and a solid, according to Andrade, is that the amplitude of molecular motion in the former is so large that molecules may collide. Osida [7] proposed a model for the thermal conductivity of dielectric liquids in which the electronic contribution of heat transmission is insignificant, similar to Andrade's theory of liquid viscosity. Osida assumed that heat is exchanged in the presence of a temperature gradient when molecules contact due to their vibration, transmitting their translational and rotational energy. Mohanty [8] investigated the link between thermal conductivity and liquid viscosity based on the theoretical results by Andrade and Osida, deriving an equation that relates both transport properties. He proposed modify this equation after an evaluation of this relationship for a small number of liquids, assuming that it would need to be corrected.

Nowadays, nanofluids, suspensions of nanometric materials in fluids, have emerged as alternative media for heat transfer applications. Although the increasing number of contributions to the understanding of the physical mechanisms behind the modification of their transport properties being reported in the literature, there are still many open questions which need to be further investigated. Correspondingly, we ensemble a novel understanding of the relevant transport properties of nanofluids on earlier works on molecular [5, 7, 8] and ionic liquids [9]. A new relationship was proposed, investigated and assessed by literature data for $MgO/n\text{-}C_{14}$ [10] Ag/PEG400 [11], TiO_2/H_2O [12] and $Al_2O_3/([C_2mim][CH_3SO_3]:H_2O)$ [13−14] nanofluids.

2. Foundations

As previously stated, Andrade [5] proposed a theory of the viscosity of liquids based on the solid state rather than the kinetic theory of gases, arguing that the main difference between solids and liquids is the amplitude of molecular motion. Based on these assumptions, it was proposed that the viscosity of a liquid near the melting point can only be estimated using experimental constants [5]. Due to their vibrations at every extreme libration, there is a transfer of momentum between molecules in neighbouring layers at this temperature. Therefore, assuming a one-third probability of a molecule oscillating along each spatial axis, the following equation for viscosity at the melting point was proposed by Andrade:

$$\eta = \frac{4}{3}\frac{\nu m}{\sigma} \tag{1}$$

in which ν, m, and σ are the frequency of the molecular vibration, the mass of the liquid and the mean distance between molecule centres, respectively.

On the other hand, Osida [7] proposed an identical model for the thermal conductivity of liquids based on the assumption that heat is carried when translational and/or rotational energy is transferred owing to molecule interactions under a temperature gradient. Omitting the internal energy of the molecules, it is straightforward to assume that every molecule has six degrees of freedom, and that its mean energy is $3kT$, where k is Boltzmann's constant. The total transported amount of energy by all the molecules of a liquid results from integrating the energy of a single molecule for all angles and lengths where the energy takes places. As Fourier's law can be applied, the thermal conductivity can be expressed as [7]:

$$\lambda = \frac{4k\nu}{\sigma} \tag{2}$$

From the above-mentioned works by Andrade [5] and Osida [7], Mohanty [8] approached a relationship between the viscosity and the thermal conductivity of liquids, derived from Eqs. (1) - (2):

$$\frac{m\lambda}{\eta} = 3k \tag{3}$$

Multiplying both sides by the Avogadro's number N:

$$\frac{M_w\lambda}{\eta} = 3Nk \tag{4}$$

in which $M_w = N \cdot m$ stands for the molecular weight. Eq. (4) is directly applicable to ideal gases, so a reformulation must be handled to adapt to different thermodynamic states. Accordingly, Mohanty [8] proposed a simple relationship for liquids based on Eq. (4) from the experimental observation of thermal conductivity and viscosity of different fluids:

$$\frac{M_w\lambda}{\eta} = \text{constant} \tag{5}$$

Actually, this relationship does not hold constant for all liquids. Subsequently, Tomida *et al.* [9] empirically found that $M_w\lambda/\eta$ decreases with increasing molecular weight for a set of *n*-alkanes and ionic liquids.

3. Novel understanding of the transport properties of nanofluids

Considering the particular case of nanofluids, *i.e.*, biphasic systems of well-dispersed solid nanomaterials within a base fluid, a new and useful relationship on transport properties is here introduced:

$$M_{nf}\left(\frac{\lambda_{nf}}{\lambda_{bf}}\right)\left(\frac{\eta_{nf}}{\eta_{bf}}\right)^{-1} = AM_{nf} - B \tag{6}$$

where M_{nf} refers to the molecular weight of the nanofluids, defined as follows:

$$M_{nf} = x_{np}M_{np} + (1 - x_{np})M_{bf} \tag{7}$$

in which x is the nanoparticle molar fraction, while the subscripts 'nf', 'np', and 'bf' refer to nanofluid, nanoparticles and base fluid, respectively.

The left-term of Eq. (6) will be hereinafter named as Nanofluid Ratio, *NR*. This ratio balances the thermal conductivity enhancement with the penalty of the increase of viscosity. There are two possible *NR* trends, increasing and decreasing with M_{nf}, since the relationship between ϕ_m and M_{nf} is different depending on the relationship between M_{np} and M_{bf}, in agreement with Eq. (7). Therefore, when $M_{np} > M_{bf}$, ϕ_m increases with M_{nf}. On the contrary, the opposite trend occurs for $M_{np} < M_{bf}$. Eq. (6) can describe these contrary linear tendencies.

Concerning the coefficients in Eq. (7), they are positive when $M_{np} < M_{bf}$ while negative when $M_{np} > M_{bf}$. The coefficient A indicates how *NR* varies with the nanofluid molecular weight. The coefficient B indicates the values of *NR* at molecular weight equal to 0, so their values are not relevant for any physical analysis purposes. Although, the coefficient A allows further discussion if it is expressed as follows:

$$A = \frac{\partial NR}{\partial M_{nf}} = \left(\frac{\lambda_{nf}}{\lambda_{bf}}\right)\left(\frac{\eta_{nf}}{\eta_{bf}}\right)^{-1} + M_{nf}\frac{\partial}{\partial M_{nf}}\left[\left(\frac{\lambda_{nf}}{\lambda_{bf}}\right)\left(\frac{\eta_{nf}}{\eta_{bf}}\right)^{-1}\right] \tag{8}$$

The first term of the right-side of Eq. (8) is the ratio between the enhancement of the thermal conductivity against the penalty of the increase of the viscosity (*i.e.*, the *NR*), and the second term is the variation of *NR* with M_{nf}. Therefore, the variation of the ratio between $\lambda_{nf}/\lambda_{bf}$ and η_{nf}/η_{bf} with the nanofluid molecular weight gives the sign of the coefficient A, the different situations for whole possible nanofluids are considered and summarized in Table 1. A coefficient cannot be zero since the transport properties of any substance have not null values. Another restriction comes from the relationship between the molecular weights of the constitutive materials: negative values are not possible for nanofluids with $M_{np} < M_{bf}$, whereas positive values cannot be neither found when dispersions fulfil $M_{np} > M_{bf}$. This consequence occurs because the second term in the right-side of Eq. (8) always prevail over the first term.

$|A| > 1$ is the most common situation in terms of the proposed model. This is due to the usual behaviour in the literature involves that the enhancement of the thermal conductivity increases slower than the penalty of the viscosity with increasing nanofluids molecular weight. Absolute A values of 1 entails λ-enhancements equal η-penalties for all nanofluid molecular weights. On the other hand, $|A| < 1$ infers the ideal conditions for nanofluids from the heat transfer point of view, because λ-enhancements grows faster than η-penalties with increasing M_{nf}. Additionally, it must be taken into account that these different outlines also depend on the two possible relationships between M_{np} and M_{bf}, as above-mentioned in this section.

The x-intercepts of the linear fittings allow to identify a molecular weight for each nanofluid set that may be understood as a 'limit' nanofluid molecular weight, $M_{nf,0}$, (or the corresponding maximum nanoparticle mass fraction, $\phi_{m,max}$). This point could indicate the hypothetical concentration from which the nanofluid behaves as a solid according to this proposed relationship. Along these lines, it must be noted that Eq. (6) can only be applied under the supposition of Newtonian behaviour throughout the entire nanoparticle mass fraction range. This parameter can be considered as a practical tool for an adequate design of nanofluids for heat transfer applications, allowing a potential estimation of the available nanoparticle mass fraction ranges.

Table 1: Possible scenarios for nanofluids depending on *A* values from the proposed relationship, Eq. (6).

	M dependence on *A*		ϕ_m dependence on *A*		$\frac{\partial}{\partial M_{nf}}\left(\frac{\lambda_{nf}/\lambda_{bf}}{\eta_{nf}/\eta_{bf}}\right)$		λ-enhancement vs. η-penalty variation
	$M_{np}<M_{bf}$	$M_{np}>M_{bf}$	$M_{np}<M_{bf}$	$M_{np}>M_{bf}$	$M_{np}<M_{bf}$	$M_{np}>M_{bf}$	
$0<\lvert A\rvert<1$	↑	↓	↓	↑	>0	<0	$\frac{\partial(\lambda_{nf}/\lambda_{bf})}{\partial\phi_m}>\frac{\partial(\eta_{nf}/\eta_{bf})}{\partial\phi_m}$
$\lvert A\rvert=1$					0	0	$\frac{\lambda_{nf}}{\lambda_{bf}}=\frac{\eta_{nf}}{\eta_{bf}},\ \forall\phi_m$
$\lvert A\rvert>1$					>0	<0	$\frac{\partial(\lambda_{nf}/\lambda_{bf})}{\partial\phi_m}<\frac{\partial(\eta_{nf}/\eta_{bf})}{\partial\phi_m}$

4. Application to different nanofluids

The reliability of the proposed model was verified with experimental data from the literature of four differentiated nanofluid sets. Hence, MgO/*n*-C_{14} [10], Ag/PEG400 [11], TiO_2/H_2O [12], and Al_2O_3/([C_2mim][CH_3SO_3]:H_2O) [13–14] were selected with the aim to study a wide variety of base fluids and due to the availability of reliable experimental data of thermal conductivity and viscosity from the same laboratory or samples. Fig. 1 depicts the analysis of such nanofluids in terms of Eq. (6). A single point corresponds to a nanofluid sample at a given temperature and nanoparticle mass fraction.

As can be seen in Fig. 1, all isotherms and studied concentrations fall onto a unique linear relationship for each nanofluid set in agreement with the non-temperature dependency of both the enhancement in the thermal conductivity and the penalty of the viscosity increment reported in the corresponding studies [10-14]. Therefore, *NR* and M_{nf} were correlated according to the proposed Eq. (6). Table 2 encloses the *A* and *B* coefficients determined by means of a least-squares method, as well as the standard deviation and coefficient of determination R^2. Indeed, the coefficients of determination of the fitting for all these nanofluids are better or equal to 0.90.

The two possible *NR* trends discussed in the previous section (increasing and decreasing with M_{nf}) can be observed in Fig. 1. MgO/*n*-C_{14}, Ag/PEG400, and Al_2O_3/([C_2mim][CH_3SO_3]:H_2O) exhibit positive trend while TiO_2/H_2O just the opposite, this effect being applicable to all nanoparticle mass fraction range. This inverse effect is since the relationship between ϕ_m and M_{nf} is different depending on the relationship between M_{np} and M_{bf}, in agreement with Eq. (7). Therefore, when $M_{np} > M_{bf}$, ϕ_m increases with M_{nf} as for TiO_2/H_2O. On the contrary, the opposite trend occurs for MgO/*n*-C_{14}, Ag/PEG400, and Al_2O_3/([C_2mim][CH_3SO_3]:H_2O) sets. Eq. (6) can describe these contrary linear tendencies.

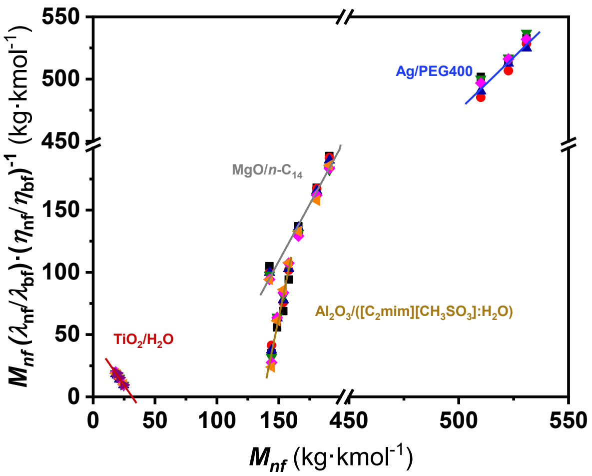

Fig. 1: Nanofluid Ratio as a function of the molecular weight of MgO/n-C_{14} [10] (shadowed in green), Ag/PEG400 [11] (shadowed in red), TiO_2/H_2O [12] (shadowed in grey), and Al_2O_3/([C_2mim][CH_3SO_3]:H_2O) [13-14] (shadowed in blue) nanofluids at different temperatures: 283.15 K (■); 293.15 K (●); 303.15 K (▲); 313.15 K (▼); 323.15 K (◆); 333.15 K (◀); and 343.15 K (▶). Linear regressions based on Eq. (6) (—).

As shown in Table 2, similar absolute A values were obtained for all the analysed nanofluid sets, excepting for Al_2O_3/([C_2mim][CH_3SO_3]:H_2O) dispersions. According to the relationship here proposed, this set would be the less worth as advanced material from heat transfer application perspectives. This can be explained by the fact that the chemical structure of the ionic liquid favours the stabilization of nanoparticles [13], leading to superior growths of the η-penalty compared to the other analysed nanofluids, triggering the higher absolute A value.

Table 2: Temperature and mass fraction ranges, coefficients A and B, 'limit' nanofluid molecular weight, maximum nanoparticle mass fraction, standard deviation, and coefficients in Eq. (6) for MgO/n-C_{14} [10], Ag/PEG400 [11], TiO_2/H_2O [12], and Al_2O_3/([C_2mim][CH_3SO_3]:H_2O) [13-14] nanofluids.

	TiO_2/H_2O	**Al_2O_3/([C_2mim][CH_3SO_3]:H_2O)**	**MgO/n-C_{14}**	**Ag/PEG400**
***T* range** (K)	293.15-343.15	283.15-333.15	283.15-333.15	283.15-323.15
ϕ_m range	0.01-0.35	0.01-0.15	0.01-0.10	0.001-0.0114
A	-1.44±0.06	4.88±0.23	1.83±0.06	1.71±0.16
B (kg·kmol^{-1})	-45.36	668.39	165.51	380.21
$M_{nf,0}$ (kg·kmol^{-1})	31.53	136.97	90.38	221.81
$\phi_{m,0}$	0.55	0.39	0.31	0.36
s (kg·kmol^{-1})	0.68	5.9	5.4	5.4
R^2	0.97	0.95	0.98	0.90

The obtained limit nanofluid molecular weights, $M_{nf,0}$ and their corresponding maximum nanoparticle mass fraction, $\phi_{m,max}$, for MgO/n-C_{14}, Ag/PEG400, TiO_2/H_2O, and Al_2O_3/([C_2mim][CH_3SO_3]:H_2O) are also enclosed in Table 2. Accordingly, maximum nanoparticle mass fractions of 31 wt%, 36 wt%, 39 wt%, and 55 wt% were obtained for MgO/n-C_{14}, Ag/PEG400, Al_2O_3/([C_2mim][CH_3SO_3]:H_2O), and TiO_2/H_2O nanofluids, respectively. The highest $\phi_{m,max}$ value corresponds to TiO_2/H_2O nanofluids, the set with lowest absolute A value. Furthermore, it is also significant that no relationship between $M_{nf,0}$ (or $\phi_{m,max}$) and M_{np} and/or M_{bf} was disclosed.

5. Conclusion

A new relationship based on transport properties of nanofluids was proposed, which balances the thermal conductivity enhancement with the penalty of the increase of viscosity, based on the theories of Andrade, Osida, and Mohanty. This proposed relationship allows the description of the transport properties of a given nanofluid for all isotherms and concentrations with a single straight-line correlation. Literature data for MgO/*n*-C_{14}, Ag/PEG400, TiO_2/H_2O, and Al_2O_3/([C_2mim][CH_3SO_3]:H_2O) nanofluid sets were used to evaluate the reliability of the relationship, obtaining coefficients of determination higher than 0.90. All nanofluids exhibit similar trends excepting TiO_2/H_2O. However, its opposite behaviour can be also described by the proposed relationship. The reported results evidence that this proposal offers an advanced understanding of transport properties of nanofluids with respect to the established literature, constituting and advanced innovative tool for the design of new nanofluids for heat transfer applications. Further advancements should be integrated, especially with the significant support of theoretical and/or numerical studies.

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