The interfacial layer effect on thermal conductivity of CNT nanofluids

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We formulate a model to predict the thermal conductivity of carbon nanotube nanorefrigerants. The interfacial layer has proved to be a significant factor responsible for the anomalous thermal conductivity enhancement of these nanofluids. The present model predicts the thermal conductivity in accordance with the experimental results with mean deviation only of 1.5%. A comparison with other models has also been made.

Keywords: Carbon nanotubes, heat transfer, interfacial nanolayer, nanofluid, thermal conductivity.

CARBON nanotubes (CNTs) have been the focus of great attention because of their distinctive structure and significant electrical and mechanical properties. These find a number of applications, including nanobearings, nanotweezers, etc.[1,2]. CNTs have unusually high thermal conductivity ranging from 2000 to 7000 $Wm^{-1} K^{-1}$ and a high aspect ratio given by $a_r = l_{CNT}/d_p$ (ref. 3). Hence it is expected that their colloidal dispersions in conventional thermal base fluids (CNT nanofluids) would exhibit enhanced thermal conductivity. A significant increase in the literature has been reported by considering the CNT geometry and volume fraction apart from the other factors. Enhanced energy transport is a remarkable feature of liquids with dispersed CNTs[4,5]. The thermal conductivity of MWCNT-poly (α-olefin) oil nanofluid shows an enhancement of more than 150% with addition of just 1.0 vol% CNTs[5]. Their improved thermal performances could find applications in energy systems such as power generation, transportation and air conditioning. In addition, microelectronics is gaining popularity with the increasing demand of energy saving and better efficiency in the industrial sectors[2].

Published results and models[5–7] confirm that the effective thermal conductivity increases with the volume fraction of nanoparticles. However, none of the models is able to properly account for the anomalous increase in thermal conductivity of CNT-based nanofluid systems. Some of the models take into account various parameters like thermal conductivity of the base fluid, thermal conductivity of CNT, their volume fraction, etc. However, few consider the effect of interfacial layer around the CNT nanoparticle[4]. The models which consider the interfacial layer concept are available for the nanofluid systems containing spherical nanoparticles, but none takes into account the cylinder or wire shape of the nanoparticle together with the interfacial layer effect.

Since various refrigerants have nearly the same value of thermal conductivity, R113 ($Cl_2FC\text{-}CClF_2$) has been chosen for this study to reflect all such nanorefrigerants[8]. This communication deals with the development of a theoretical model for a series of CNT-based nanofluids dispersed in R113 by taking into account two important mechanisms of heat conduction – heat transfer facilitated by the interfacial nanolayer and convective heat transfer due to the motion of nanoparticles in the base fluid.

When CNTs are dispersed in the nanorefrigerant, the adsorption of the nanorefrigerant on the surface of CNT results in the formation of a nanolayer in which the base molecules get arranged in a manner which results in their density intermediate between the medium and the particle. This essentially enforces the inclusion of nanolayer as an important parameter for studying the effective thermal conductivity of the nanofluid.

The interfacial layer model has been put forward by a number of research groups as an important mechanism behind the anomalous thermal conductivity enhancement[9–15]. The interfacial layer around the nanoparticle is thought to be an orderly arrangement of the fluid molecules around the nanoparticle. This orderly arrangement has an intermediate thermal conductivity between the nanoparticle and the base fluid. The nanoparticle is assumed to have the structure as shown in Figure 1. The nanoparticle is assumed to be cylindrical in shape with heat being conducted along the length of the particle. The nanoparticles are assumed to be distributed uniformly in the base fluid.

The thermal conductivity of the nanolayer varies with distance r from inner radius r_p of the nanoparticle to the entire thickness of the interfacial layer around the nanoparticle before it becomes equal to k_f at the interface. Here, the empirical formulation is introduced based on the assumptions that thermal conductivity is equal to thermal conductivity of the nanoparticle k_p at the inner

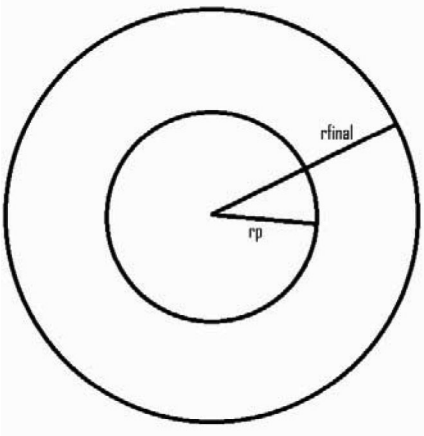

Figure 1. The cross-section area of the cylindrical nanoparticle.

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interface and at the outer interface it is equal to thermal conductivity of the base fluid k_f so that[16]

$$k(r) = \begin{cases} k_p & r \le r_p \\ f(r) & r_p \le r \le r_{final} \\ k_f & r_{final} \le r \end{cases} \quad (1)$$

Here, $f(r)$ is assumed to have the following empirical forms

$$f(r) = k_f + \frac{(k_p - k_f)}{\tanh m} \tanh\left(m \frac{(r_{final} - r)}{(r_{final} - r_p)} \right),$$

$$f(r) = k_f + \frac{(k_p - k_f)}{(1 - e^m)} \left[1 - \exp\left(m \frac{(r_{final} - r)}{(r_{final} - r_p)} \right) \right], \quad (2)$$

where m is a real positive integer. Since both the above forms satisfy the boundary conditions given in eq. (1), both forms have been tried. The corresponding thermal conductivity profile within the interfacial layer is displayed in Figure 2.

From the plot, it is evident that the variation in $f(r)$ is in conformation with the boundary conditions that for $r = r_{final} = r_p * d$, $f(r)$ must reduce to the thermal conductivity of base fluid k_f, whereas for $r = r_p$, the thermal conductivity should be the same as that of the particle, i.e. k_p. Figure 2 shows thermal conductivity profile of interfacial layer for different values of m. For $m \ge 5.0$, we observe the thermal conductivity profile to approach a behaviour similar to a step function, which points to the situation that there is no formation of interfacial layer around the dispersed nanoparticles in the base fluid. It sharply decreases from k_p to k_f either at the particle–layer interface as seen for tangent hyperbolic function or at the layer–liquid interface as seen for the exponential function. Thus, one does not expect m to take on large values. In fact, m can be interpreted to include the effect of nature and type of packing of atoms in the interfacial layer formed around the particle. Also, for smaller values of m, the calculated results are not found to vary at all. Moreover, it also corresponds to a variation in thermal conductivity profile which incorporates the structural behaviour of the interfacial layer very well. Thus, for simplicity, we chose the value of m to be 1.

The resistance offered by the nanolayer to the thermal conductivity of the fluid as a whole is given by[10]

$$R_L = \frac{1}{\pi K_1} \left[\frac{l}{r_p^2} - \frac{(l + 2\delta)}{(r_{final})^2} \right], \quad (3)$$

where $l \times r_p$ are the dimensions of the nanoparticle. The resistance is related to the thermal conductivity distribution between r_p and r_{final} as

$$R_L = \int_{r_p}^{r_{final}} \frac{dr}{2\pi r_p (r_p + l) f(r)}. \quad (4)$$

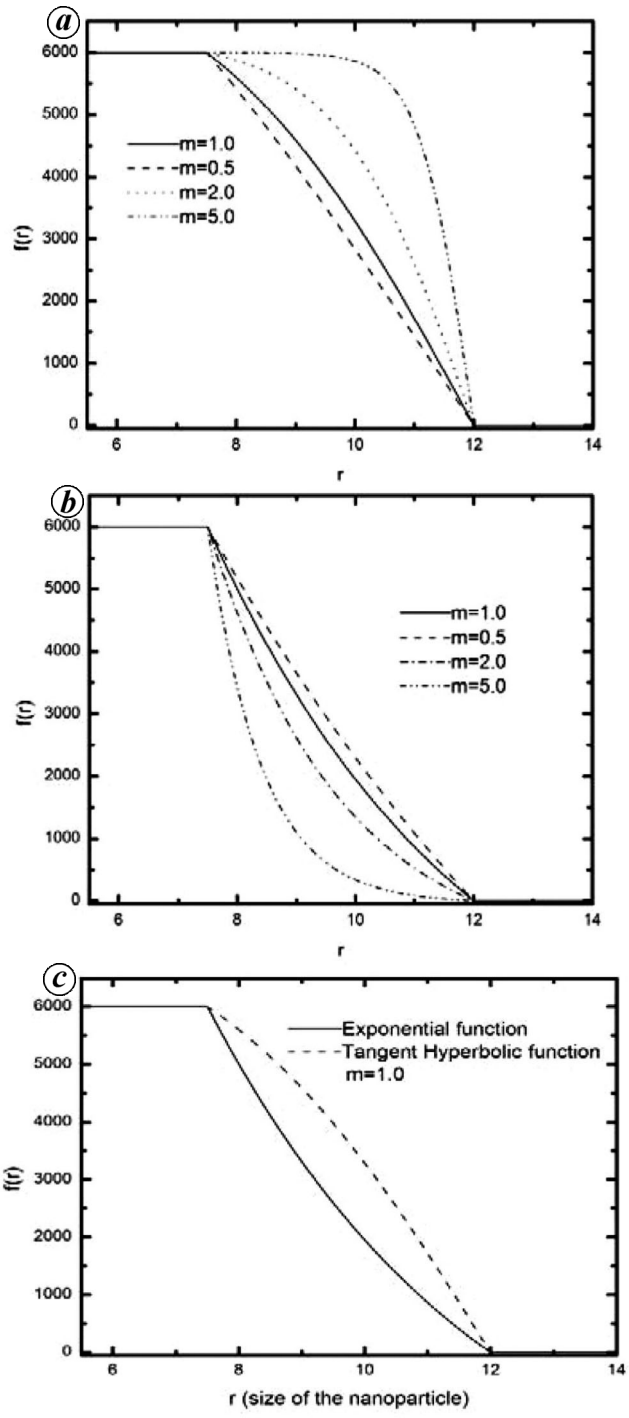

Figure 2. Thermal conductivity profile of the nanolayer with (***a***) tangent hyperbolic function, (***b***) exponential function and (***c***) their comparison for $m = 1$.

Using the two preceding equations we get

$$k_1 = \frac{\left[\frac{l}{r_p^2} - \frac{(l+2\delta)}{(r_{final})^2}\right]}{\int_{r_p}^{r_{final}} \frac{dr}{2r_p(r_p+l)f(r)}}. \quad (5)$$

The resistance offered by the base fluid is

$$R_f = \frac{1}{4\pi h r_p^2 d^2}, \quad (6)$$

where h is the heat transfer coefficient introduced by Pasrija *et al.*[17] given by

$$h = \frac{k_f}{d_p}(1 + A\,\mathrm{Re}^n\,\mathrm{Pr}^{1/3}\,\phi_{eq}). \quad (7)$$

The parameter n in the above equation is a constant which depends on the nature of the nanofluid used. The value of coefficient A is 4×10^4. The values of n have to be modified from those given by Prasher *et al.*[17], as they did not include the nanolayer part in their calculations. It gives the Reynold's number contribution to the Brownian motion.

The net resistance offered is additive in nature and is given by

$$R_{eff} = R_L + R_f. \quad (8)$$

The effective thermal conductivity is given by the following equation

$$R_{eff} = \frac{1}{4\pi k_e r_p}\left(1 - \frac{1}{R^+}\right), \quad (9)$$

where in case of a cylindrical nanoparticle, $R^+ = r_0/r_p$ taken as the function of equivalent volume fraction ϕ_{eq} as the base fluid molecules are large in number[9] and is given by

$$R^+ = \frac{1}{\sqrt{\phi_{eq}}}. \quad (10)$$

From the above equations, the effective thermal conductivity ratio is given by

$$\frac{k_e}{k_f} = \frac{1}{4}\left(1 - \sqrt{\phi_{eq}}\right)\left[\frac{k_f}{K_L}\left(\frac{l_p}{r_p} - \frac{l_p + 2\delta}{r_p d^2}\right) + \frac{k_f}{h r_p d^2}\right]^{-1}. \quad (11)$$

The volume fraction of a cylindrical particle is given by

$$\phi = u\pi r_p^2 l, \quad (12)$$

where l is the length of the particle, r_p is the radius of the cross-section of the nanoparticle and u is the particle number. So the equivalent volume fraction of the nanoparticle which is surrounded by the nanolayer is given by

$$\varphi_{eq} = u\pi r_{final}^2 (l + 2\delta). \quad (13)$$

Here $l + 2\delta$ represents the increased length of CNT and u is the particle number. Also, $l(\mu m) + 2*\delta(nm) \sim 1\ \mu m$. Therefore

$$\varphi_{eq} = u\pi r_p^2 d^2 l = \varphi d^2. \quad (14)$$

The Hamilton–Crosser model[18] gives the modified form of Maxwell's model[19], which has a shape factor for considering the particles to be cylindrical in shape. The expression for thermal conductivity according to this model is given by

$$\frac{k_{eff}}{k_f} = \frac{\alpha + (n-1) - (n-1)(1-\alpha)\phi}{\alpha + (n-1) + (1-\alpha)\phi}, \quad (15)$$

where n is the shape factor and α is the ratio of k_p and k_f.

The Yu and Choi model[20] gives the thermal conductivity of the nanofluid as

$$k_{eff}/k_f = \left(1 + \frac{3\psi^{-\alpha}\phi C}{1 - \phi C}\right), \quad (16)$$

with $\alpha = 1.55$, ψ is a parameter on sphericity and C is a parameter on thermal conductivity of CNT.

Hosseini *et al.*[21] gave a model based on dimensionless groups for calculating the effective thermal conductivity of nanofluids. According to this model

$$\frac{k_{eff}}{k_f} = 1 + m\left(\frac{1}{d}\right)^{\alpha} (a_r)^{\beta} (\upsilon_c)^{\gamma}, \quad (17)$$

where m is a factor depending on the properties of the CNT and the interfacial shell, while α, β and γ are empirical constants determined from experimental data and calculated using least square regression method.

Jiang *et al.*[8] presented a modified form of Yu and Choi[20] to explain the effective thermal conductivity of nanofluids and used the parameter α as obtained by regression analysis on experimental data of thermal

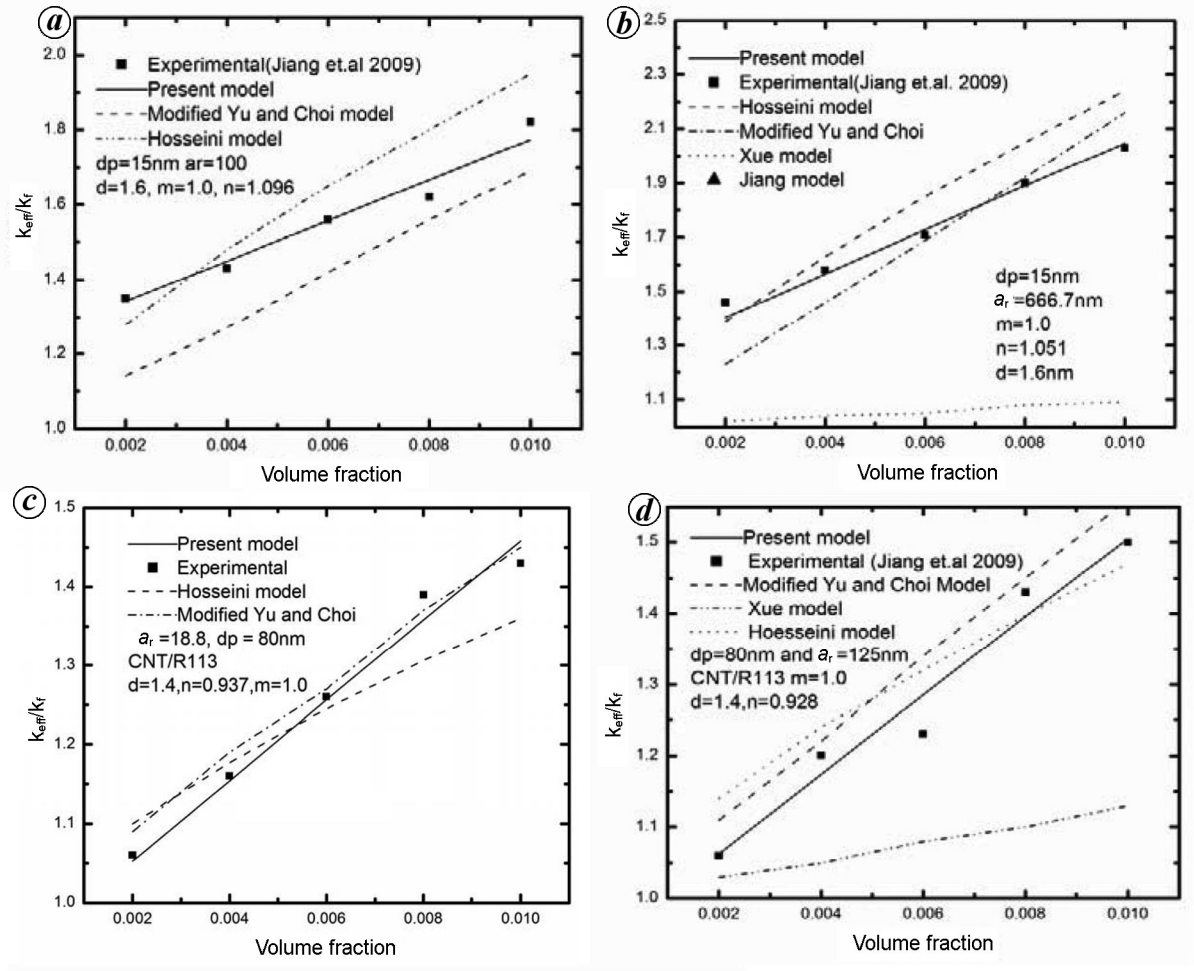

Figure 3. Effective thermal conductivity of carbon nanotube nanofluid with: ***a***, d_p = 15 nm, a_r = 100 nm, d = 1.6 and n = 1.096; ***b***, d_p = 15 nm, a_r = 666–7 nm, d = 1.6 and n = 1.051; ***c***, d_p = 80 nm, a_r = 18.8 nm, d = 1.4 and n = 0.937; ***d***, d_p = 80 nm, a_r = 125 nm, d = 1.4 and n = 0.928.

conductivities of CNT-R113 nanorefrigerant. It is given by

$$\alpha = 1.55 + 16.7(d_p / l)^{0.71}, \quad (18)$$

where d_p the diameter of the CNT nanoparticle.

Figure 3 shows a comparison between the results obtained from various models and the presented model for various CNT-R113 suspensions. Jiang *et al.*[8] gave a modified Yu and Choi model (using eq. (8)), which is reported to be better than the Yu and Choi model[20]. Figure 3 shows a comparison of the present model with the modified Yu and Choi model as well as the model by Hosseini *et al.*[21] of dimensionless groups. These figures clearly bring out the success of our model even for different aspect ratio and size of the nanoparticles.

The thermal conductivity of CNT nanorefrigerants has been studied as a function of CNT volume fraction using eq. (11). The variation is shown in Figure 3. The effective thermal conductivity increases with increase in volume fraction of the nanoparticle and the results of this model match well with the experimental results given by Jiang *et al.*[8]. The results obtained have also been compared with the other models like that of Yu and Choi[20], Hosseini *et al.*[21] and Xue[22]. The values of n and d are obtained using least square fitting method. We get d = 1.6, when the value of diameter of cross-section of the nanoparticle (d_p) is 15 nm, while the value of d = 1.4 when d_p is 80 nm. This shows that interfacial layer thickness is a function of diameter or size of the nanoparticle. The different values of the parameter n and d are given in Table 1. The different values of n for different systems show that Brownian motion depends on the nature of the particle and the system under study.

It is also evident from the table that the value of interfacial layer thickness is dependent on size of the particle. Smaller nanoparticles have slightly more thickness of the interfacial layer. The present model can further help in predicting the interfacial layer thickness required

Table 1. Different combinations of parameters d_p, a_r, d and n for CNT nanofluids

d_p	a_r	d	n
15	100	1.6	1.096
15	666.7	1.6	1.051
80	18.8	1.4	0.937
80	125	1.4	0.928

for a particular application for which the system is being used.

The mean and maximum deviations in our model are 1.5% and 4% respectively while those reported by Hosseini *et al.*[21] are 5.35% and 10.35%; Yu and Choi[20] are 15.6% and 27.4%, and Jiang *et al.*[8] are 5.5% and 15.8% respectively. This shows that the present model gives better results than the theoretical models listed above.

A semi-empirical predictive model containing three adjustable parameters using Brownian motion concept along with the formation of nanolayer was developed. The values of the parameters are found using least square fitting with the available experimental results. The model consists of the effect of the required effective parameters like thermal conductivities of the pure nanorefrigerant and the CNT nanoparticle, volume fraction of the nanoparticles, interfacial layer thickness, size of the nanoparticle and its aspect ratio. This simple formulation of the model for the systems under study provides excellent agreement with the available experimental results. This model gives better predictions compared to the existing models for nanofluids containing nanoparticles with cylindrical morphology. Hence the following conclusions can be drawn from the present analysis:

(i) The interfacial layer concept and the concept of convective heat transfer caused by Brownian motion of the fluid particles prove significant in explaining the anomalous enhancement in thermal conductivity of the CNT-based nanofluids.

(ii) The interfacial layer thickness and hence effective thermal conductivity depend on the diameter as well as the aspect ratio of CNT.

(iii) The present model is able to predict the enhancement in thermal conductivity more accurately than the existing models[8,20,21]. It has a mean deviation of 1.5%.

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