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Thermal conductivity of nanofluids: influence of particle shape

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The paper proposes a modified Maxwell formula applied to the calculation of the thermal conductivity of nanofluids. It is shown that the use of elongated particles or chains of nanoparticles leads to a significant increase in thermal conductivity. Theoretical estimates based on the proposed model are in good agreement with experimental data.

Keywords: Thermal conductivity, nanofluids, elongated particles, chains of nanoparticles, Maxwell formula.

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1. One of the approaches to improve thermal conductivity [1] is the replacement of conventional oils and water with nanofluids containing solid phase nanoparticles. The experimentally obtained improvement of thermal conductivity was described well in the model of two-phase liquid–solid particles system proposed by Maxwell [2,3]. Maxwell formula to calculate the thermal conductivity coefficient follows from the precise solution to the thermal conductivity equation. It is often used for spherical particles, however the formula is applicable to particles of any shape. This requires the formfactor to be calculated. To avoid these calculations, which are not always finite, modified formulae are often introduced, including „manmade“ additions to the formula for spherical particles.

Record-high thermal conductivity of diamond and industrial-scale production of diamond nanoparticles (DN) were the drivers of the attempts to create diamond nanofluids [4,5]. An improvement of thermal conductivity by 10% was achieved in nanofluids based on ethylene glycol [4] and by 5% in the nanofluid based on deionized water [5] with addition of DN up to 1% wt.

It should be noted that in [4] an attention was paid to an experimentally obtained improvement of thermal conductivity that could not be described in the two-phase system model — by Maxwell formula.

In this work, an explanation is given why Maxwell formula does not yield results corresponding to the experimentally obtained values of the thermal conductivity coefficient in nanofluids with DN [4,5] and carbon nanotubes (CNT) [6], and a theory is proposed for these nanofluids that yields results matching with experiments.

Based on this theory, a forecast is made that to improve thermal conductivity, it is reasonable to create nanofluids that contain nanoparticles with high aspect ratio between length and width.

2. The mathematical model of heat propagation in a medium with inclusion of particles in the case under consideration can be built on the basis of solution to the thermal conductivity equation for one particle of ellipsoid shape (see, for example, [7,8]). The modelling consider circular ellipsoids with aspect ratio equal to n.

Topological features of bodies are taken into account through the use of formfactor. The formfactor in the model of elongated ellipsoids is as follows

$$F = \frac{1}{2}\int_0^\infty \frac{dx}{(1+n^2x)(1+x)^{3/2}}. \qquad (1)$$

If $n = 1$, the formfactor is $F = 1/3$, which corresponds to a spherical particle.

By integrating we get

$$F = \frac{1}{n^2-1}\left[\frac{n}{2\sqrt{n^2-1}}\ln\frac{n+\sqrt{n^2-1}}{n-\sqrt{n^2-1}} - 1\right]. \qquad (2)$$

This formula can be simplified for $n > 6$:

$$F \approx [\ln(2n) - 1]/n^2. \qquad (3)$$

Formfactors of particles with aspect ratios $n < 6$ are given in the Table below.

Formula to calculate the effective thermal conductivity coefficient of a nanofluid κ_{pf} (see [8]) that replaces in the adopted model the Maxwell formula, for the case when the nanoparticle material with a concentration of φ_c has a thermal conductivity coefficient of κ_p, while the liquid has a thermal conductivity coefficient of κ_f, can be written as

Formfactors of nanoparticles

n	F
1	0.333
2	0.175
3	0.110
4	0.076
5	0.056
6	0.043

follows

$$\kappa_{pf} = \kappa_f \frac{1 + \left(\frac{\kappa_p}{\kappa_f} - 1\right)[F + (1-F)\varphi_c]}{1 + \left(\frac{\kappa_p}{\kappa_f} - 1\right)F(1-\varphi_c)}. \qquad (4)$$

Here, as usual, an assumption is made that the heat distribution remains unchanged if particles do not contact each other, which corresponds to the case of low φ_c concentrations. If the formfactor is $F = 1/3$, then formula (4) is the same as the Maxwell formula.

Further in the text the $K = \kappa_{pf}/\kappa_f$ parameter is used that represents the increase in thermal conductivity of fluid due to introduction of nanoparticles.

3. The information on the use of CNTs to improve the effective thermal conductivity coefficient κ_{pf} for different liquids are put together in the review [9]. According to [6], the most promising material to convert the solar energy to thermal energy is $Li_2CO_3{-}K_2CO_3{-}Na_2CO_3$ ternary carbonate with a component mass ratio of 4:4:2. For the temperature range of 500–560°C thermal conductivity of this ternary carbonate is $\kappa_f = 0.65{-}0.70\,\mathrm{W/(K\cdot m)}$. To ease the creation of suspension with CNT, surface-active agents are added to the liquid ternary carbonate, however they improve thermal conductivity insignificantly: thermal conductivity of the liquid without CNTs $\kappa_f = 1.0{-}1.1\,\mathrm{W/(K\cdot m)}$ is more than three orders of magnitude less than the thermal conductivity of CNTs themselves, which is $\kappa_p \approx 3000{-}3500\,\mathrm{W/(K\cdot m)}$.

Let us assume for the modelling that CNTs correspond to circular ellipsoids that have one of their semi-axis (length) l n times larger than two other (width) d. Using the data of [6], we get that expression (3) is applicable. As a matter of fact, $n = l/d \approx (0.5{-}2.0\,\mu\mathrm{m})/(20{-}30\,\mathrm{nm}) = 100{-}20 \gg 10$.

Thus, for the case considered in [6], we can determine from (2) and (3) the value of formfactor, and then use (4) to get the thermal conductivity coefficient

$$K = 1 + \frac{\varphi_c n}{3[\ln(2n) - 1]}. \qquad (5)$$

For the concentrations of 1% wt. used in [6] and at densities of the ternary carbonate specified there, and for the CNTs used in this study with a density of $1.8\,\mathrm{kg/m^3}$ we determine the concentration of CNTs equal to $\varphi_c = 1.2\%$ vol. By substituting all the above-mentioned values, we get that the effective thermal conductivity coefficient of the ternary carbonate with surface-active agents that contains CNTs in a concentration of φ_c should not be less than $\kappa_{pf} \approx 1.40\,\mathrm{W/(K\cdot m)}$.

The theoretic value calculated in this way matches to the majority of experimental results given in [6] (for various temperatures and with different surface-active agents) to the accuracy of $> 90\%$. The record-setting experimental values of 1.63 and $1.62\,\mathrm{W/(K\cdot m)}$ are obtained (see [6]) when needle-like structures are formed in the nanofluid.

4. An evident geometric analog for CNTs are chains of nanoparticles. Recently it was shown (see [10–12]) that diamond nanoparticle form chains in hydrosols of detonation-synthesized nanodiamond (DND) particles.

In [4] values are given for the effective thermal conductivity coefficient κ_{pf} of ethylene glycol (EG) containing low concentrations (fractions of percent) of DNDs with a size of $\sim 11\,\mathrm{nm}$ in water and 18 nm in toluene.

Similar values are given in [5] for deionized water, with diamond nanoparticles of size 4–5 nm dispersed in the deionized water and functionalized by chemical addition of groups compatible with the host liquid.

The experimental values obtained in both [4] and [5] are considerably higher than the thermal conductivity coefficients calculated in these works using Maxwell formula. It is likely that DNDs in EG and in water do not have spherically symmetric shape, which is assumed by this formula [2,3]. It should be noted that thermal conductivities of EG ($\kappa_f = 0.25\,\mathrm{W/(K\cdot m)}$) and water ($\kappa_f = 0.61\,\mathrm{W/(K\cdot m)}$) are by four orders of magnitude less than thermal conductivities of diamond particles ($\kappa_p \approx 1200{-}2000\,\mathrm{W/(K\cdot m)}$) and three orders of magnitude less than thermal conductivities of graphite ($100{-}350\,\mathrm{W/(K\cdot m)}$).

Let us consider the thermal conductivity of nanofluid in the case of presence of chains composed of DND particles, which are considered spherical.

The concentration of chains φ_c corresponds to the concentration of ellipsoid particles mentioned in para. 2 and that of nanotubes mentioned in para. 3. Let us write the following

$$\varphi_c = \alpha\varphi/(3n), \qquad (6)$$

where α is the fraction of DND particles included in the chains, and φ is the concentration of DND particles added to the liquid. It should be emphasized that the aspect ratio n for a chain is the same as the number of DND particles connected into the chain. Assuming isotropic the distribution of particles over directions, we can assume the portion of chains stretched along the specific direction equal to 1/3.

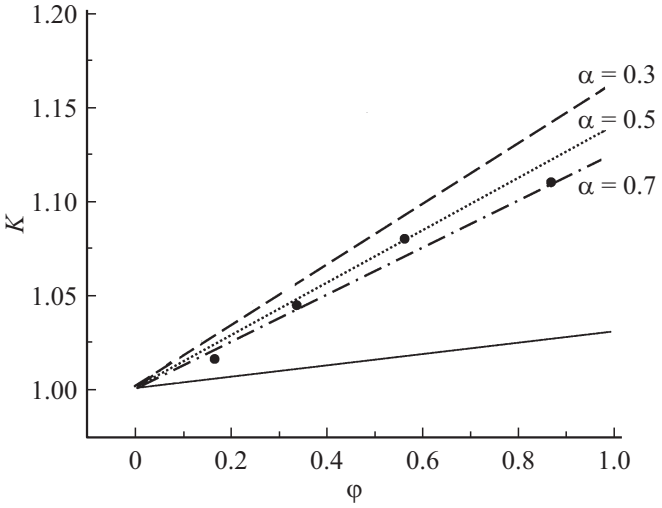
Now we can determine the formfactor from (4), and by substituting this formfactor into (3), we get

$$K = 1 + \frac{\alpha\varphi n}{3[\ln(2n) - 1]}. \qquad (7)$$

For CNT $\alpha = 1$, and expression (7) transforms to formula (5).

It is evident that chains with different lengths are involved in the process of thermal conductivity. It is logical to assume that the portion of diamond nanoparticles included in chains with pre-defined number of particles n decreases with increase in n.

Let us assume that chains with $n = 2$ contain a half of all particles included in the chains, their portion is $\alpha/2$; chains with $n = 3$ include a quarter of all particles included in the chains, etc. This descent has the property that $\sum_{m=1}^{m} \frac{1}{2^m}$ tends to unit with increase in m, which should be valid for any decrease law of chain number having n links, when



The increase in thermal conductivity of nanofluid $K = \kappa_{pf}/\kappa_f$ as compared with the thermal conductivity of fluid depending on the concentration of diamond nanoparticles φ. Parameter α is the portion of particles included in the chains. Points — experimental data from [4], solid line — calculation of K coefficient by Maxwell formula.

n increases. Then the expression for increase in thermal conductivity is as follows

$$K = \varphi \sum_{n=2}^{n} \frac{1 + \frac{\alpha n}{2^{n-1}}}{3[\ln(2n) - 1]}. \qquad (8)$$

The figure illustrates the increase in thermal conductivity of nanofluid with chains of DND nanoparticles depending on the concentration of particles φ added into the fluid, at various portions of DND particles included in chains (α). It can be seen that the best match between the experimental results and calculations taking into account the formation of chains [4,5] is observed in the case when chains are formed from 50% of diamond nanoparticles added to the fluid.

5. The geometric matching and the matching of the ratio between calorific capacities of the filler (DND or CNT) and calorific capacities of the appropriate fluids make it possible to explain the experiments of [4–6] from a single point of view. The results of calculation obtained in this work match good with the results of measurements presented in [4,5] for diamond nanoparticles in ethylene glycol and in water, and with the results presented in [6] for carbon nanotubes in the ternary carbonate.

It is shown that to improve thermal conductivity, nanofluids need to be created that ceteris paribus contain nanoparticles with high aspect ratio between length and width or form long chains.

The topological similarity of diamond nanoparticle chains and carbon nanotubes made it possible to conduct calculations by a single method using Maxwell formula for this case. The calculations did not take into account the effect of thermal conductivity decrease due to thermal resistance at the interface between the fluid and nanoparticles — the Kapitza effect. The estimates show that taking this effect into consideration does not change the qualitative result.

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Conflict of interest

The authors declare that they have no conflict of interest.

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