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The combined analysis of phonon and electron heat transfer mechanism on thermal conductivity for nanofluids

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Abstract

The paper features the mathematical model representing the analytical calculation of phonon and electron heat transfer analysis of thermal conductivity for nanofluids. The mathematical model was developed on the basis of statistical nanomechanics. We have made the detailed analysis of the influence of temperature dependence on thermal conductivity for nanofluids. On this basis are taken into account the influences such as formation of nanolayer around nanoparticles, the Brown motion of solid nanoparticles and influence of diffusive-ballistic heat transport.

The analytical results obtained by statistical mechanics are compared with the experimental data and they show relatively good agreement.

1. Introduction

Billions of years ago, when enormous quantities of energy were released after the Big Bang, the fundamental particles followed by molecules were formed into more or less complex structures according to certain coincidental events. In the period of several billion years of development, the Earth was also shaped as one of the planets in space with life on it. By some marvellous accident life was created on it, yet with a one flaw. In the process of evolution, Mother Nature formed human beings. By observing nature and through their own intelligence the human beings managed to subordinate all living beings in the process of evolution. At the same time, they also gradually learn how to exploit substances and materials. The ability of making tools and devices distinguished men from other living beings. Around 400,000 years ago, people were capable of making wooden spears and lances. They made tools and devices twice their own size. It has always been people's wish to make ever larger machines and devices. The reason is probably very simple, namely the leaders ruling at the time wanted to be ranked among the immortals. In Egypt, for example, the builders constructed pyramids in 2600 BC for the needs of the pharaohs, with the tallest being 147 m high Keops' pyramid. In 1931, the 449 m tall Empire State Building was built in New York. Currently, the last preparations are underway in Shanghai to construct a 1000 m high housing building. With the development of increasingly larger devices many inventors and scientists wished to reveal the secrets of micro cosmos. For centuries, clock makers were the most important representatives of those diminishing the size of devices. In the 17th century, the invention of the microscope opened up the way to the observation of microbes, plant and animal cells. Only in the late 20th century, micro-devices were technologically refined. Today, the size of transistors in integrated circuits is 0.18 μm and the transistors measuring 10 nm are already being developed in laboratories.

December 29, 1958 is thought to be date of the beginning of micromechanics and nanomechanics, when at the California Institute of Technology the Nobel prize winner Richard P. Feynman delivered a lecture within the Ameri-

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Nomenclature

A	Avsec model
C_p	heat capacity at constant pressure per mole
CLS	Chung–Lee–Starling
HC	Hamilton–Crosser model
k_B	Boltzmann constant
L	temperature dependent constant
l_{el}	electron mean free path
l_{ph}	phonon mean free path
Kn	Knudsen number
LJ	Lennard–Jones
M	molecular mass
N	number of molecules in system
R_m	universal gas constant
T	temperature
t	time
T^*	reduced temperature
T_c	critical temperature
v_{el}	electron speed
V	volume
V_c	critical volume
Z_{coll}	collision number
X	Xue model
α	volume fraction
β	diffusion term
ε	Lennard–Jones parameter
θ_D	Debye temperature
θ_E	Einstein temperature
λ	thermal conductivity
Λ	heat conduction transport coefficient
μ_r	relative dipole moment
κ	correction factor for hydrogen bonding effect
κ_s	shear viscosity
ρ	density
σ	Lennard–Jones parameter
σ_e	electrical conductivity
ψ	influence of polyatomic molecules
ω	acentric factor
Ω	collision integral
Ω^*	reduced collision integral
τ	relaxation time

Superscripts and subscripts

0	dilute gas state
c	critical condition
el	electron
ph	phonon
p	influence of high densities

can Physical Association. He introduced at the lecture a vision of reducing the size of machines to nano-size. At that time, professor Feynman could not see the economic implications of the devices made on the basis of nanotechnology. Nanomechanics and micromechanics are becoming increasingly important in today's industry. The concepts of invisible aircraft, pumps ... are now a reality. At the same time, problems have arisen in advanced mechanics not even dreamed of before. Thermodynamic and transport properties of a gas flowing through a tube with the diameter of a few nanometers are modelled completely differently due to a great influence of surface effects. Even classical hydromechanics is not of much help here. In addition to temperature and pressure the Knudsen number is becoming increasingly important. Euler's equation gives bad results almost over the entire range, Navier–Stokes' equation at Knudsen number 0.1 and Burnett's equation at Knudsen number 10. However, in order to analyse free molecular flow in micro and nanochannels the non-equilibrium mechanics and the original Boltzmann's equation have to be used. In this case, computation of hydromechanical problems is possible over the entire range of Knudsen, temperatures and pressures [1,2].

The term nanofluid is envisioned to describe a solid–liquid mixture which consists of a nanoparticles and a base liquid and this is one of new challenges for thermo-sciences provided by the nanotechnology. the possible application area of nanofluids is in advanced cooling systems, in micro/nano electromechanical systems ... the investigation of the effective thermal conductivity of liquid with nanoparticles attract much more interest experimentally and theoretically. The effective thermal conductivity of nanoparticle suspension can be much higher than for the fluid without nanoparticles.

2. Calculation of thermal conductivity for pure fluid [3–6]

Accurate knowledge of non-equilibrium or transport properties of pure gases and liquids, is essential for the optimum design of the different items of chemical process plants, for determination of intermolecular potential energy functions and for development of accurate theories of transport properties in dense fluids. Transport coefficients describe the process of relaxation to equilibrium from a state perturbed by application of temperature, pressure, density, velocity or composition gradients. The theoretical description of these phenomena constitutes that part of non-equilibrium statistical mechanics that is known as kinetic theory.

In the presented paper will be presented Chung–Lee—Starling model (CLS) [4,5]. Equations for the thermal conductivity are developed based on kinetic gas theories and correlated with the experimental data. The low-pressure transport properties are extended to fluids at high densities by introducing empirically correlated, density dependent functions. These correlations use acentric factor ω, dimen-

sionless dipole moment μ_r and empirically determined association parameters to characterize molecular structure effect of polyatomic molecules κ, the polar effect and the hydrogen bonding effect. In this paper are determined new constants for fluids.

The dilute gas thermal conductivity for CLS model is written as

$$\lambda = \lambda_k + \lambda_p \tag{1}$$

where

$$\lambda_k = \lambda_0\left(\frac{1}{H_2} + B_6 Y\right) \tag{2}$$

The thermal conductivity in the region of dilute gases for CLS model is written as

$$\lambda_0 = 3119.41\left(\frac{\eta_0}{M}\right)\psi \tag{3}$$

where ψ represents the influence of polyatomic energy contributions to the thermal conductivity. We used the Taxman theory. He solved the problem of influence of internal degrees of freedom on the basis of WCUB theory [3] and the approximations given by Mason and Monschick [2]. The final expression for the influence of internal degrees of freedom is represented as

$$\psi = 1 + C^*_{\text{int}} \times \left\{ \frac{0.2665 + \frac{(0.215-1.061\beta)}{Z_{\text{coll}}} + 0.28288\frac{C^*_{\text{int}}}{Z_{\text{coll}}}}{\beta + \frac{0.6366}{Z_{\text{coll}}} + \frac{1.061\beta C^*_{\text{int}}}{Z_{\text{coll}}}} \right\} \tag{4}$$

where C^*_{int} is the reduced internal heat capacity at constant volume, β is the diffusion term and Z_{coll} is the collision number. The heat capacities are calculated by use of statistical thermodynamics. The paper features all important contributions (translation, rotation, internal rotation, vibration, intermolecular potential energy and influence of electron and nuclei excitation). The residual part λ_p to the thermal conductivity can be represented with the following equation:

$$\lambda_p = \left(0.1272\left(\frac{T_c}{M}\right)^{1/2}\frac{1}{V_c^{2/3}}\right)B_7 Y^2 H_2\left(\frac{T}{T_c}\right)^{1/2} \tag{5}$$

where λ_p is in W/mK.

$$H_2 = \left\{B_1[1-\exp(-B_4 Y)]\frac{1}{Y} + B_2 G_1 \exp(B_5 Y) + B_3 G_1\right\} \times \frac{1}{B_1 B_4 + B_2 + B_3} \tag{6}$$

The constants B_1–B_7 are linear functions of acentric factor, reduced dipole moment and the association factor

$$B_i = b_0(i) + b_1(i)\omega + b_2(i)\mu_r^4 + b_3(i)\kappa, \quad i = 1, 10 \tag{7}$$

where the coefficients b_0, b_1, b_2 and b_3 are presented in the work of Chung et al. [4,5].

3. The calculation of thermal conductivity for pure solids [7–11]

3.1. Electronic contribution to the thermal conductivity

The fundamental expression for electronic contribution λ_{el} to the thermal conductivity can be calculated on the basis of the theory of thermal conductivity for classical gas:

$$\lambda_{el} = \frac{1}{3} n c_{el} v_{el} l_{el} \tag{8}$$

where c_{el} is the electronic heat capacity (per electron), n is the number of conduction electrons per volume, v_{el} is the electron speed and l_{el} is the electron mean free path. In Eq. (8) it is assumed that in temperature gradient electrons travel just the same average distance l before transferring their excess thermal energy to the atoms by collisions.

We can express the mean free path with the help of electron lifetime τ ($l_{el} = v_F \tau$):

$$\lambda_{el} = \frac{\pi^2 n k_B^2 T \tau}{3m} \tag{9}$$

With the help of Drude theory [6,7] we can express thermal conductivity as the function of electrical conductivity σ_e:

$$\lambda_{el} = \sigma_e L T \tag{10}$$

where L is the temperature dependent constant.

3.2. Phonon contribution to the thermal conductivity

It is more difficult to determine the thermal conductivity when there are non-free electrons. Solids which obey this rule we called non-metallic crystals. Because the atoms in a solid are closely coupled together, an increase in temperature, will be transmitted to the other parts. In the modern theory, heat is being considered as being transmitted by phonons, which are the quanta of energy in each mode of vibration. We can again use the expression:

$$\lambda_{ph} = \frac{1}{3} C v l \tag{11}$$

3.3. The calculation of electronic contribution using Eliashberg transport coupling function

In the book of Grimwall [9] we can find the analytical expression for the electrical conductivity σ:

$$\sigma_e = \frac{n e^2}{m_b}\left\langle \tau(\varepsilon, \vec{k}) \right\rangle \tag{12}$$

In Eq. (7) m_b represents electron band mass and τ is an electron lifetime that depends both on the direction of the wave vector $\vec{k}$ and on the energy distance ε. The brackets $\langle \cdots \rangle$ describe an average over all electron states. We can also describe the electronic part of thermal conductivity with the help of Eq. (12):

$$\lambda_{\mathrm{el}} = \frac{nk_{\mathrm{B}}T}{m_{\mathrm{b}}}\left\langle \left(\frac{\varepsilon_k - E_{\mathrm{F}}}{k_{\mathrm{B}}T}\right)^2 \tau(\varepsilon,\vec{k})\right\rangle \tag{13}$$

The lifetime for the scattering of electrons by phonons contains quantum-mechanical quantum matrix elements for the electron–phonon interaction and statistical Bose–Einstein and Fermi–Dirac factors for the population of phonon and electron states. A very useful magnitude in the context is the Eliashberg transport coupling function $\alpha^2_{\mathrm{tr}}F(\omega)$. A detailed theoretical expression is possibly to find in the work of Grimwall [9,11]. The Eliashberg coupling function allows us to write the thermal conductivity in the next expression:

$$\begin{aligned}\frac{1}{\lambda_{\mathrm{el}}} = {} & \frac{(4\pi)^2}{L_0 T\omega_{\mathrm{pl}}^2}\times\int_0^{\omega_{\max}} \\ & \times\frac{\hbar\omega/k_{\mathrm{B}}T}{[\exp(\hbar\omega/k_{\mathrm{B}}T-1)][1-\exp(-\hbar\omega/k_{\mathrm{B}}T)]} \\ & \times\left\{\left[1-\frac{1}{2\pi^2}\left(\frac{\hbar\omega}{k_{\mathrm{B}}T}\right)^2\right]\alpha^2_{\mathrm{tr}}F(\omega)\right. \\ & \left.+\frac{3}{2\pi^2}\left(\frac{\hbar\omega}{k_{\mathrm{B}}T}\right)^2\alpha^2_{\mathrm{tr}}F(\omega)\right\}\mathrm{d}\omega\end{aligned} \tag{14}$$

We can describe the phonons by an Einstein model

$$\alpha^2_{\mathrm{tr}}F(\omega) = A\delta(\omega-\omega_{\mathrm{E}}) \tag{15}$$

$$\alpha^2F(\omega) = B\delta(\omega-\omega_{\mathrm{E}}) \tag{16}$$

In Eqs. (15) and (16) are B and A constants. With the help of Eqs. (15) and (16) we can solve integral in Eq. (14):

$$\frac{1}{\lambda_{\mathrm{el}}} = k_{\mathrm{E}}C_{\mathrm{har}}(T/\theta_{\mathrm{E}})\left[\frac{A}{B}+\left(\frac{\theta_E}{T}\right)^2\frac{1}{2\pi^2}\left(3-\frac{A}{B}\right)\right] \tag{17}$$

In Eq. (17) k_{E} represents the constant, θ_{E} is the Einstein temperature and C_{har} represents the lattice heat capacity in Einstein model:

$$C_{\mathrm{har}} = 3Nk_{\mathrm{B}}T\left(\frac{\theta_{\mathrm{E}}}{T}\right)^2\frac{\exp\left(\frac{\theta_{\mathrm{E}}}{T}\right)}{\left[\exp\left(\frac{\theta_{\mathrm{E}}}{T}\right)-1\right]^2} \tag{18}$$

Motokabbir and Grimwall [10] discussed about Eq. (17) with A/B as a free parameter with assumption that $A/B \approx 1$.

3.4. The phonon contribution to thermal conductivity

In an isotropic solid we can express the thermal conductivity as the integral over ω containing the phonon density of states $F(\omega)$:

$$\lambda_{\mathrm{ph}} = \frac{N}{3V}v_{\mathrm{g}}^2\int_0^{\omega_{\max}}\tau(\omega)C(\omega)F(\omega)\mathrm{d}\omega \tag{19}$$

where v_{g} is some average phonon group velocity, C is the heat capacity of a single phonon mode and the ratio N/V is the number of atoms per volume.

A relaxation time can be expressed as the ratio of a mean free path to a velocity, so that the thermal conductivity can be expressed as

$$\lambda_{\mathrm{ph}} = \frac{N}{3V}v_{\mathrm{g}}\int_0^{\omega_{\max}} l(\omega)C(\omega)F(\omega)\mathrm{d}\omega \tag{20}$$

The crucial point in Eq. (20) is the determination of relaxation time. If we consider scattering in and out of state 1 we can with help of quantum mechanics describe $\tau(1)$:

$$\frac{1}{\tau(1)} = \frac{2\pi}{\hbar}\sum_{2,3}|H(1,2,3)|^2\frac{n(2)n(3)}{n(1)} \tag{21}$$

$$|H(1,2,3)|^2 = A\frac{\hbar^2\gamma^2\Omega_{\mathrm{a}}^{1/3}}{3MN}\frac{\omega_1\omega_2\omega_3}{v_{\mathrm{g}}^2} \tag{22}$$

The evaluation of $\tau(1)$ in Eq. (21) requires a summation over modes 2 and 3. This cannot be done analytically, so it is not possible to give a closed-form expression for the temperature dependence of the thermal conductivity valid at all temperatures.

For the low temperature region (where the temperature is lower than Debye temperature θ_{D}) we have used the solution:

$$\lambda_{\mathrm{ph}} = \lambda_0\exp\left(-\frac{\theta_{\mathrm{D}}}{T}\right) \tag{23}$$

where λ_0 is the constant.

For the high temperature region ($T \gg \theta_{\mathrm{D}}$) the solution of Eq. (23) gives the result:

$$\lambda_{\mathrm{ph}} = \frac{B}{(2\pi)^3}\frac{M\Omega_{\mathrm{a}}^{1/3}k_{\mathrm{B}}^3\theta_{\mathrm{D}}^3}{\hbar^3\gamma^2T} \tag{24}$$

where B is dimensionless constant, Ω_{a} is atomic volume and γ is the Grüneisen constant. The relation between the Einstein and Debye temperature may be written as

$$\theta_E = (0.72\ldots0.75)\theta_{\mathrm{D}} \tag{25}$$

4. The calculation of thermal conductivity for nanofluids [11–37]

In nanoparticle fluid mixtures, other effects such as microscopic motion of particles, particle structures and surface properties may cause additional heat transfer in nanofluids. Nanofluids also exhibit superior heat transfer characteristics to conventional heat transfer fluids. One of the main reasons is that suspended particles remarkably increase thermal conductivity of nanofluids. The thermal conductivity of nanofluid is strongly dependent on the nanoparticle volume fraction. So far it has been an unsolved problem to develop a sophisticated theory to predict thermal conductivity of nanofluids. The presented paper is the attempt to calculate thermal conductivity of nanofluid analytically. Hamilton and Crosser developed the macroscopic model for the effective thermal conductivity of two-component mixtures as a function of the conductivity of the pure materials, the composition and shape of

dispersed particles. The thermal conductivity can be calculated then with the next expression [12–34]:

$$\lambda = \lambda_0 \left\{ \frac{\lambda_p + (n-1)\lambda_0 - (n-1)\alpha(\lambda_0 - \lambda_p)}{\lambda_p + (n-1)\lambda_0 + \alpha(\lambda_0 - \lambda_p)} \right\} \tag{26}$$

where λ is the mixture thermal conductivity, λ_0 is the liquid thermal conductivity, λ_p is the thermal conductivity of solid particles, α is the volume fraction and n is the empirical shape factor given by,

$$n = \frac{3}{\Psi} \tag{27}$$

where Ψ is sphericity, defined as the ratio of the surface area of a sphere (with a volume equal to that of a particle) to the area of the particle. The volume fraction α of the particles is defined as

$$\alpha = \frac{V_p}{V_0 + V_p} = n\frac{\pi}{6}d_p^3 \tag{28}$$

where n is the number of the particles per unit volume and d_p is the average diameter of particles.

An alternative expression for calculating the effective thermal conductivity of solid–liquid mixtures was introduced by Wasp [34]:

$$\lambda = \lambda_0 \left\{ \frac{\lambda_p + 2\lambda_0 - 2\alpha(\lambda_0 - \lambda_p)}{\lambda_p + 2\lambda_0 + \alpha(\lambda_0 - \lambda_p)} \right\} \tag{29}$$

Comparison between Eqs. (26) and (29) show that Wasp model is a special case with the sphericity of 1.0 of the Hamilton and Crosser model. From the literature [14–34] we can find some other models (Maxwell, Jeffrey, Davis, Lu-Lin...) with almost identical analytical results.

In nanofluids is many possible mechanisms for the anomalously increased effective thermal conductivity:

– Influence of nanolayer thickness
– Hyperbolic heat conduction
– Brownian motion
– Particle driven or thermally driven natural convection
– Hyperbolic thermal natural convection

4.1. The influence of nanolayer around nanoparticle

The HC model gives very good results for particles larger than 13 nm. For smaller particles the presented theory gives wrong results with the deviation more than 100% in comparison with experimental results. The presented theoretical models for the calculation of the thermal conductivity for nanofluids are only dependent on the thermal conductivity of the solid and the liquid and their relative volume fraction, but not on particle size and the interface between particles and the fluid. For the calculation of effective thermal conductivity we have used Xue theory [18], based on Maxwell theory and average polarization theory. Because the interfacial shells are existed between the nanoparticles and the liquid matrix, we can regard both the interfacial shell and the nanoparticle as a complex nanoparticle. So the nanofluid system should be regarded as the complex nanoparticles dispersed in the fluid. We assume that λ is the effective thermal conductivity of the nanofluid, λ_c and λ_m are the thermal conductivity of the complex nanoparticles and the fluid, respectively. The final expression of Xue [18] model (X) is expressed with the next equation:

$$9\left(1 - \frac{\alpha}{\lambda_r}\right)\frac{\lambda - \lambda_0}{2\lambda + \lambda_0} + \frac{\alpha}{\lambda_r}\left[\frac{\lambda - \lambda_{c,x}}{\lambda + B_{2,x}(\lambda_{c,x} - \lambda_e)} + 4\frac{\lambda - \lambda_{c,y}}{2\lambda + (1 - B_{2,x})(\lambda_{c,y} - \lambda)}\right] = 0 \tag{30}$$

$$\lambda_{c,j} = \lambda_1 \frac{(1 - B_{2,j})\lambda_1 + B_{2,j}\lambda_2 + (1 - B_{2,j})\lambda_r(\lambda_2 - \lambda_1)}{(1 - B_{2,j})\lambda_1 + B_{2,j}\lambda_2 - B_{2,j}\lambda_r(\lambda_2 - \lambda_1)} \tag{31}$$

We assume that the complex nanoparticle is composed of an elliptical nanoparticle with thermal conductivity λ_2 with halfradii of (a, b, c) and an elliptical shell of thermal conductivity λ_1 with a thickness of t. In Eqs. (30) and (31) λ_r represents the spatial average of heat flux component. For simplicity we assume that all fluid particles are balls and all the nanoparticles are the same rotational ellipsoid.

We have used the model of Yu and Choi [23] that the nanolayer of each particle could be combined with the particle to form an equivalent particle and that the particle volume concentration is so low that there is no overlap of those equivalent particles. On this basis we can express the effective volume fraction:

$$\alpha_e = \alpha\left(1 + \frac{h}{r}\right)^3 \tag{32}$$

where h represents the liquid layer thickness. We have also made the assumption that equivalent thermal conductivity of the equivalent particles has the same value as the thermal conductivity of particle. On the basis of all the presented assumptions we have derived the new model (RHC) for thermal conductivity for nanofluids:

$$\lambda = \lambda_f \left\{ \frac{\lambda_{pt} + (n-1)\lambda_f - (n-1)\alpha_e(\lambda_f - \lambda_{pt})}{\lambda_{pt} + (n-1)\lambda_f + \alpha_e(\lambda_f - \lambda_{pt})} \right\} \tag{33}$$

4.2. Hyperbolic heat conduction

Heat transport in nanoparticles is predominantly by electron and crystal vibrations, depends on material. Macroscopic theories assume diffusive heat transport with Laplace equation [41]:

$$\rho c_p \frac{\partial T}{\partial t} = \lambda \nabla^2 T + \dot{q} \tag{34}$$

where $\dot{q}\,dx\,dy\,dz$ represent the internal energy source term. In the steady state and with boundary conditions we can express the upper equation in the next expression:

$$\vec{J}_Q = -\lambda \vec{\nabla} T \tag{35}$$

where J_Q is the heat flux. In crystalline nanoparticles heat is carried out by phonons, such phonons are created at random, propagate directions, they are scattered by each other. With the simplest theory due to Debye, the mean free path of the phonon is given by expression [14]:

$$l_{\mathrm{ph}} = \frac{10aT_{\mathrm{m}}}{\gamma T} \tag{36}$$

where T_{m} is the melting point, a is the lattice constant and γ is the Grüneisen parameter. For typical nanoparticle such as Al_2O_3 at room temperature we obtain the result that the mean phonon free path is 35 nm [12]. Due to this reason, phonons cannot diffuse in the 10 nm particles but must move ballistically across the particle.

In metals, the heat is primarily carried by electrons, which also exhibit diffusive motion at the macroscopic level. Due to Drude formula we can express the mean electron free path as [11]:

$$l_{\mathrm{el}} = \frac{9.2r_{\mathrm{s}}^2}{\rho_{\mathrm{el}}\ [\mu\Omega\mathrm{cm}]}10^{-9}\ [\mathrm{m}] \tag{37}$$

where ρ_{el} is the electrical resistivity and r_{s} is the dimensionless parameter. For Cu is l_{el} 350 nm, for Al is l_{el} 65 nm. Due to this reason, electrons cannot diffuse in the 10 nm particles but must move ballistically across the particle.

The mentioned analysis has shown that the assumption that the heat transport developed on the basis of diffusive phenomena is invalid. It is very difficult to demonstrate how ballistic heat transport could be more effective than a very fast diffusion transport [24,38]. In the future, we will take into account the ballistic heat transfer phenomena in nanoparticles too on the basis of Boltzmann law [38].

The ratio between the mean free path l and the characteristic length L is called the Knudsen number [40]:

$$Kn = \frac{l}{L} \tag{38}$$

In the nanotechnology could be possibly that the Knudsen number becomes comparable or higher that 1. As the result the heat transport is no longer diffusive but becomes ballistic. In that situation the usual Fourier law describing diffusive transport must be generalized to cover conventionally the mentioned transition [39].

$$q = \lambda\frac{\Delta T}{L}\ \text{(diffusive transport)} \tag{39}$$

$$q = \Lambda\Delta T\ \text{(ballistic transport)} \tag{40}$$

where λ represents the thermal conductivity and Λ the heat conduction transport coefficient. The presented phenomena we can solve on many different ways:

- direct application of universal Boltzmann equation
- the application of extended irreversible thermodynamics
- application of dual time lag equations
- numerical computer simulations of heat transport on the basis of lattice theory consideration into account slow and fast process of heat transport at the same time

In the presented paper we have focused on the extended irreversible thermodynamics theory.

$$q = \lambda(T, l/L)\frac{\Delta T}{L} \tag{41}$$

The limiting behaviour of this generalized conductivity to recover expressions in the suitable situations should be:

$$\lambda(T, l/L) \to \lambda(T)\ \text{for}\ l/L \to 0 \tag{42}$$

$$\lambda(T, l/L) \to \frac{\lambda(T)}{a}\frac{L}{l} \equiv \Lambda(T)L\ \text{for}\ l/L \to \infty \tag{43}$$

where a is the constant depending on the system. On that basis we obtain the next equation [40] for the determination of real thermal conductivity in all regimes:

$$\lambda(\omega, k) = \frac{\lambda(T)}{1 + \mathrm{i}\omega\tau_1 + \cfrac{k^2 l_1^2}{1+\mathrm{i}\omega\tau_2+\cfrac{k^2 l_2^2}{1+\mathrm{i}\omega\tau_3+\cfrac{k^2 l_3^2}{1+\mathrm{i}\omega\tau_4}}}} \tag{44}$$

If we choose $l_n^2 = \alpha_{n+1}l^2$ with $\alpha_n = n^2[(2n+1)(2n-1)]^{-1}$. The presented assumption is of interest because it corresponds to a detailed analysis of photon or phonon heat transport [40]. The presented assumption leads to the next expression:

$$\lambda(T, l/L) = \frac{3\lambda}{Kn^2}\left[\frac{Kn}{\tan^{-1}(Kn)} - 1\right] \tag{45}$$

For the determination of effective thermal conductivity due to electron heat transport and depending on Knudsen number, we have used the same method as it is presented in Eq. (45).

4.3. Brownian motion

In many authors (Koo, Kumar...) is postulated that the enhanced thermal conductivity of a nanofluid is mainly, due to Brownian motion which produces micro mixing. Because of the small size of the particles in the fluids, additional energy term can arise from motions induced by stochastic (Brownian) and interparticle forces. Motion of particles cause microconvection that enhances heat transfer:

$$\text{Koo etal. [35,36]}: \lambda_{\mathrm{Brownian}} = 5\times10^4\beta\alpha\rho_{\mathrm{l}}c_{\mathrm{l}}\sqrt{\frac{\kappa T}{\rho_{\mathrm{p}}D}}f,$$

$$f = (-6.04\alpha + 0.4705)T + (1722.3\alpha - 134.63) \tag{46}$$

$$\text{Kumar etal.[32]}: \lambda_{\mathrm{Brownian}} = c\frac{2k_{\mathrm{B}}T}{\pi\eta d_{\mathrm{p}}^2} \tag{47}$$

Wang et al. [19]:

The heat transfer enhancement due to the Brownian motion can be estimated with the known temperature of the fluid and size of the particles. The increase of thermal conductivity due to the rotational and translational motion of spherical particle:

$$\lambda_{\text{Brownian}} = \lambda_f \alpha \left(\frac{1.17(\lambda_p - \lambda_f)^2}{(\lambda_p + 2\lambda_f)^2} + 5(0.6 - 0.028) \frac{(\lambda_p - \lambda_f)}{(\lambda_p + 2\lambda_f)^2} \right) \times Pe_f^{1.5} + (0.0556 Pe_t + 0.1649 Pe_t^2 - 0.0391 Pe_t^3 + 0.0034 Pe_t^4)\lambda_f \quad (48)$$

Prasher [33]:

$$\lambda = \lambda_0 \left\{ \frac{\lambda_p + (n-1)\lambda_0 - (n-1)\alpha(\lambda_0 - \lambda_p)}{\lambda_p + (n-1)\lambda_0 + \alpha(\lambda_0 - \lambda_p)} \right\} \left(1 + \frac{\text{RePr}}{4} \right) \quad (49)$$

$$\text{Re} = \frac{1}{v} \sqrt{\frac{18 k_B T}{\pi \rho d}} \quad (50)$$

where v is the kinematic viscosity of fluid. In our case we have used the model for Brownian motion from Prasher[33]. We have slightly corrected the Prasher equation into the next expression:

$$\lambda = \lambda_0 \left\{ \frac{\lambda_p + (n-1)\lambda_0 - (n-1)\alpha(\lambda_0 - \lambda_p)}{\lambda_p + (n-1)\lambda_0 + \alpha(\lambda_0 - \lambda_p)} \right\} \times (1 + C\text{Re}^m \text{Pr}^n) \quad (51)$$

where C represents the fitting parameter.

5. Results and comparison with experimental data

In the presented paper we will show analytical computations for the mixtures between copper nanoparticles and ethylene glycol and also for the mixture between aluminum oxide (Al_2O_3) nanoparticles and water. The copper nanoparticles dispersed in the fluid are very interesting for nanofluid industrial application due to very high thermal conductivity in comparison with copper or aluminum oxides. In our case we have used experimental results from the literature [15] where copper average nanoparticles diameter is smaller than 10 nm.

Fig. 1 shows temperature influence of electron mean free path and Knudsen number. Fig. 2 shows the analytical calculation of mixture between ethylene glycol and copper nanoparticles for thermal conductivity ratio. The results for thermal conductivity obtained by Avsec model (A) model show relatively good agreement. Thermal conductivity predicted by Hamilton–Crosser (HC) model give much lower values as Experimental results (Exp). Fig. 2 is developed on the theory that the nanolayer thickness is one of the reasons for heat transfer enhancement. The theory was made on the assumption that the nanolayer thickness is one of the most important contribution [12] in very small nanoparticles ($d \ll 10$ nm). At the some time we have taken into account in A model the influence on ballistic and diffusive heat conduction and the influence of Brownian motion. On the assumption that the nanolayer thickness is the most important contribution we have obtained also very successful analytical results for viscosity and thermodynamic properties in nanofluids at room temperature in comparison with experimental data [12]. Unfortunately

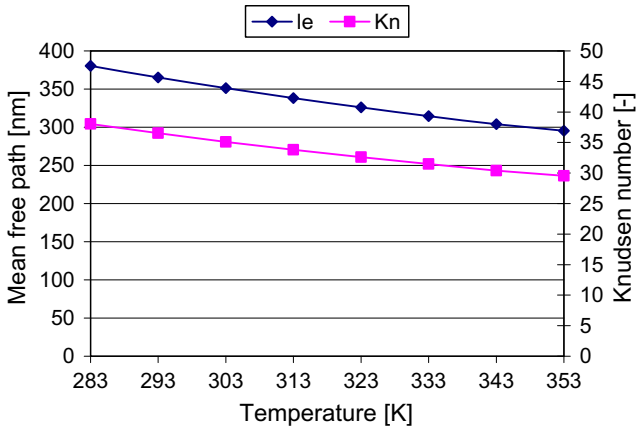


Fig. 1. Mean electron free path and Knudsen number for Cu nanoparticles with the average diameter 10 nm.

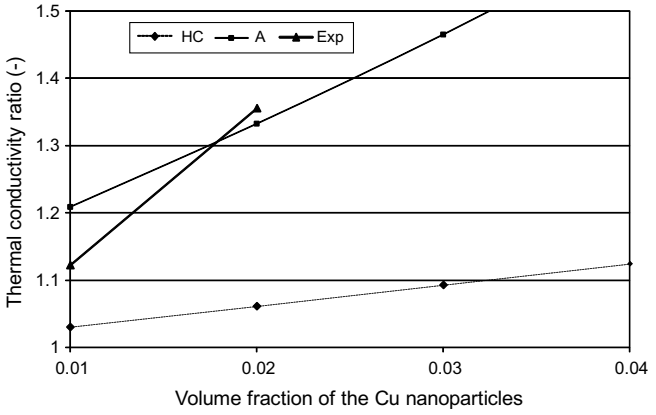


Fig. 2. Thermal conductivity of mixture copper nanoparticles + ethylene glycol at various composition at 303 K.

the nanofluid theory developed only on the theory, that the nanolayer thickness is the reason for heat transfer enhancement did not give the satisfactory results for the temperature dependence problems. In principle, it is possi-

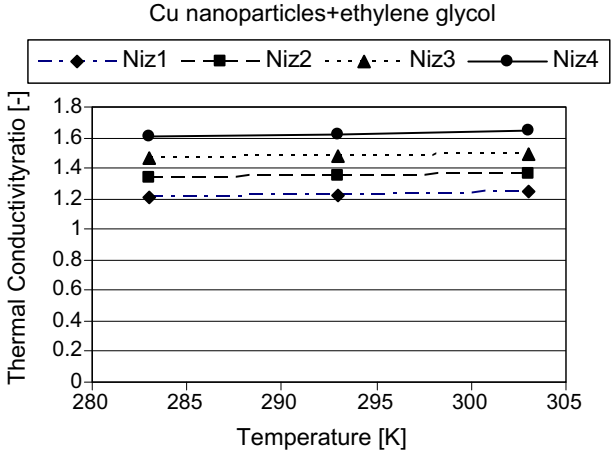


Fig. 3. Analytical prediction of thermal conductivity of mixture copper nanoparticles + ethylene glycol at various composition at various temperatures (Niz1-$\alpha = 0.01$, Niz2-$\alpha = 0.02$, Niz3-$\alpha = 0.03$, Niz4-$\alpha = 0.04$).

bly that the nanolayer thickness is temperature dependent, but up to this date we did not find successful theory or experimental results. Fig. 3 shows the analytical prediction with A model the temperature influence of thermal conductivity of mixture between copper nanoparticles and ethylene glycol as the reference fluid.

Figs. 4–7 show the comparison between our new model (A) and experimental results [26] for Al_2O_3 nanoparticles and water as the reference fluid. Figs. 4–7 show the thermal conductivity ratio in dependence of temperature field. The average diameter of Al_2O_3 nanoparticles is 38.4 nm. Fig. 4 shows the predictions for Brownian motion velocity and Knudsen number in dependence of temperature field [42,43].

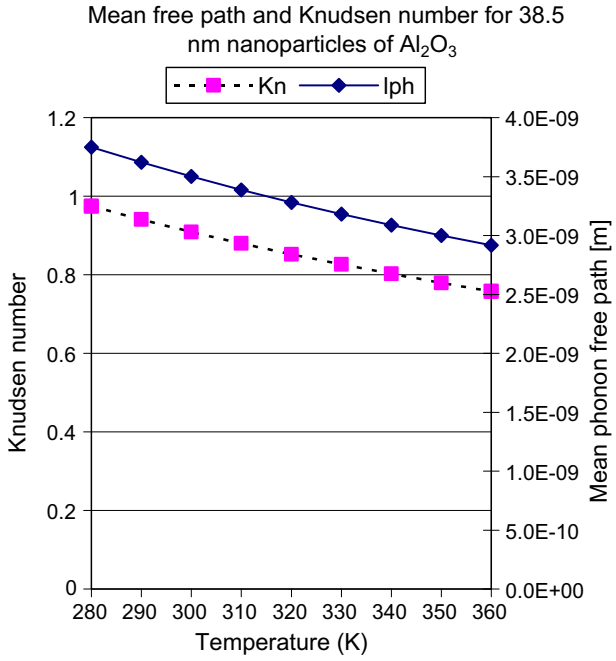


Fig. 4. Knudsen number and mean free phonon path for Al_2O_3 nanoparticles with average diameter 38.5 nm.

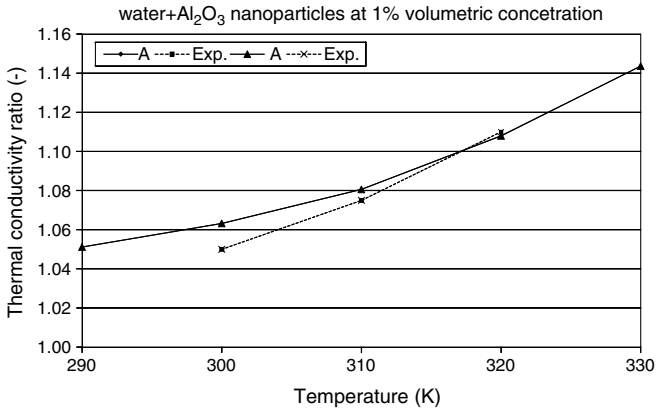
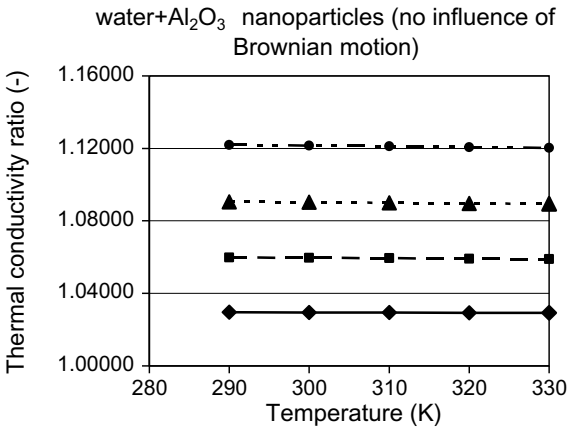


Fig. 5. Thermal conductivity of water + Al_2O_3 nanoparticles with average diameter 38.4 nm at 1% of volume concentration of nanoparticles.



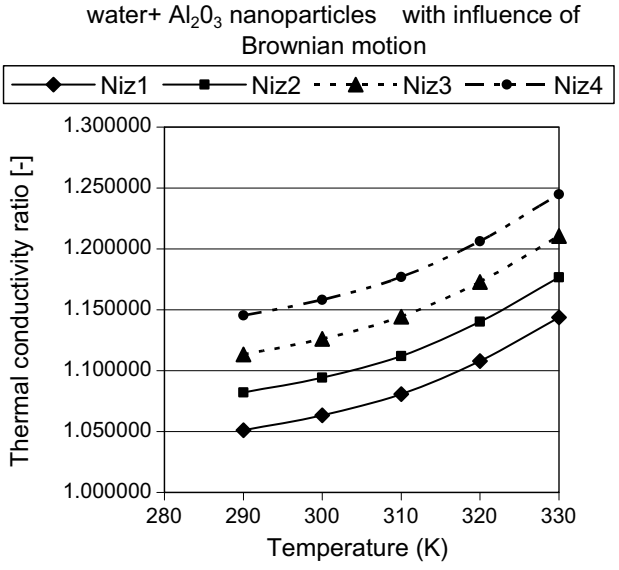


Fig. 6. Analytical prediction of thermal conductivity and influence of Brownian motion in the mixture water × Al_2O_3 nanoparticles with A model (Niz1-$\alpha = 0.01$, Niz2-$\alpha = 0.02$, Niz3-$\alpha = 0.03$, Niz4-$\alpha = 0.04$).

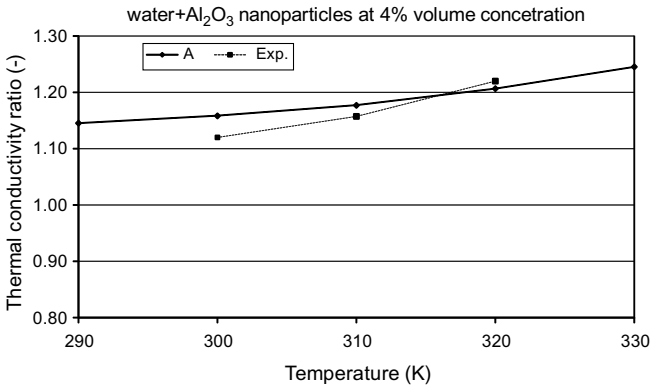


Fig. 7. Thermal conductivity of water + Al_2O_3 nanoparticles with average diameter 38.4 nm at 4% of volume concentration of nanoparticles.

Fig. 8 shows the thermal conductivity in the dependence of temperature field and Knudsen number.

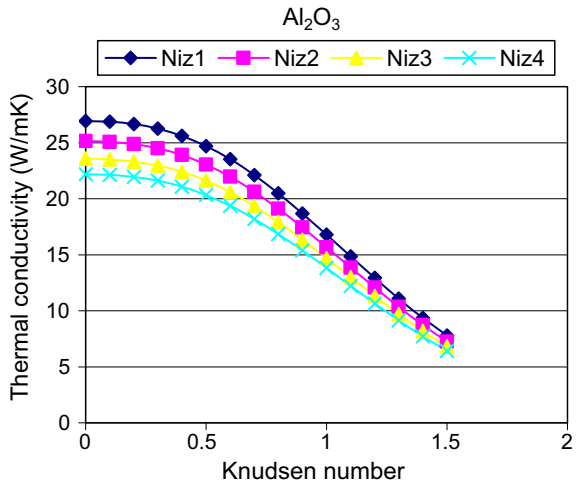


Fig. 8. Thermal conductivity in dependence of Knudsen number (Niz1-$T = 280$ K, Niz2-$T = 300$ K, Niz3-$T = 320$ K, Niz4-$T = 340$ K).

The detailed analysis shows that the presented mathematical model predicts the thermal conductivity very accurately in dependence of volume fraction of nanoparticles and temperature field.

6. Conclusion

The paper presents the mathematical model for computation of transport properties for nanofluids. The analytical results are compared with the experimental data and show relatively good agreement

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