

The calculation of thermal conductivity, viscosity and thermodynamic properties for nanofluids on the basis of statistical nanomechanics

Jurij Avsec*, Maks Oblak

University of Maribor, Faculty of Mechanical Engineering, Smetanova 17, 2000 Maribor, P.O. Box 224, Slovenia

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Abstract

The paper features the mathematical model of calculation of thermophysical properties for nanofluids on the basis of statistical nanomechanics. Calculation of properties for nanofluids for real substances is possible by the classical and statistical mechanics. Classical mechanics has no insight into the microstructure of the substance. Statistical mechanics, on the other hand, calculates the properties of state on the basis of molecular motions in a space, and on the basis of the intermolecular interactions. The equations obtained by means of classical thermomechanics are empirical and apply only in the region under observation. The main drawback of classical thermomechanics is that it lacks the insight into the substance of microstructure. Contrary to classical mechanics, statistical mechanics calculates the thermomechanic properties of state on the basis of intermolecular and intramolecular interactions between particles in the same system of molecules. It deals with the systems composed of a very large number of particles.

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

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1. Introduction

One of the great scientific and technical advancement at the end of 20th century and at the start of the 21st century is the creation of nanomaterials and nanotechnology. The area which cover all important problems from that field is called in the broadest sense the mechanics. Regarding the cross sectional diameter we can divide mechanics into some subdisciplines [1]:

macromechanics: 10^{-4} – 10^{-5} m,
mesomechanics: 10^{-5} – 10^{-7} m,
micromechanics: 10^{-7} – 10^{-8} m,
nanomechanics: 10^{-8} – 10^{-9} m.

Since the atomic level (interatomic distance in a crystal lattice) has an order of one to several Å (10^{-10} m) the nanolevel is restricted to 10^{-9} m.

Nanomechanics and micromechanics are becoming increasingly important in today's industry. The concepts of invisible aircraft, pumps, etc. 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 nanometres 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 nonequilibrium mechanics and the original Boltzmann's equation

* Corresponding author. Tel.: +386 2 2207752; fax: +386 2 2207990.
E-mail address: jurij.avsec@uni-mb.si (J. Avsec).

Nomenclature

C_p	heat capacity at constant pressure per mole	X	Xuan model
C_V	heat capacity at constant volume	β	diffusion term
C_{el}	electronic heat capacity	ε	Lennard-Jones parameter
C_{har}	lattice heat capacity	η	viscosity
CLS	Chung–Lee–Starling	θ_D	Debye temperature
CYJ	revised Cotterman model	θ_E	Einstein temperature
E	Eliashberg coupling function	λ	thermal conductivity
FPC	fluid properties calculator	μ_r	relative dipole moment
HC	Hamilton–Crosser model	κ	correction factor for hydrogen bonding effect
k_B	Boltzmann constant	κ_s	shear viscosity
L	temperature dependent constant	ρ	density
l_{el}	electron mean free path	ρ^*	reduced density
LJ	Lennard-Jones	σ	Lennard-Jones parameter
M	molecular mass	σ_e	electrical conductivity
N	number of molecules in system	ψ	influence of polyatomic molecules
R_m	universal gas constant	ψ_i	molar fraction of component i
RHC	revised Hamilton–Crosser model	ω	acentric factor
RD	relative deviation	Ω	collision integral
RW	revised Ward model	Ω^*	reduced collision integral
T	temperature	<i>Superscripts and subscripts</i>	
T^*	reduced temperature	0	dilute gas state
T_c	critical temperature	c	critical condition
v_{el}	electron speed	el	electron
V	volume	ph	phonon
v_c	critical volume	p	influence of high-densities
W	Ward model		
Z_{coll}	collision number		

have to be used. In this case, computation of hydromechanical problems is possible over the entire range of Knudsen, temperatures and pressures [1].

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.

Calculation of properties for nanofluids for real substances is possible by the classical and statistical mechanics. Classical mechanics has no insight into the microstructure of the substance. Statistical mechanics, on the other hand, calculates the properties of state on the basis of molecular motions in a space, and on the basis of the intermolecular interactions. The equations obtained by means of classical thermodynamics are empirical and apply only in the region under observation. The main drawback of classical thermodynamics is that it lacks the insight into the substance of microstructure. Contrary to classical mechanics,

statistical mechanics calculates the thermomechanic properties of state on the basis of intermolecular and intramolecular interactions between particles in the same system of molecules. It deals with the systems composed of a very large number of particles.

In this paper we determined new constants for fluids. The results of the analysis are compared with experimental data, and shows a relatively good agreement.

2. Calculation of thermal conductivity

2.1. Calculation of thermal conductivity for pure fluid [2–5]

Accurate knowledge of nonequilibrium 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 nonequilibrium statistical mechanics that is known as kinetic theory.

In this paper, a comparative study will be presented with respect to Chung–Lee–Starling model (CLS) [6,7]. 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 , dimensionless 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:

$$\lambda_0 = 3119.41 \left(\frac{n_0}{M} \right) \psi, \tag{3}$$

where ψ represents the influence of polyatomic energy contributions to the thermal conductivity. We used the Taxman theory [2]. He solved the problem of influence of internal degrees of freedom on the basis of WCUB theory [8] and the approximations given by Mason and Monchick [2–8]. The final expression for the influence of internal degrees of freedom is represented as:

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

where C_{int}^* is the reduced internal heat capacity at constant volume, β is 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/m K.

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

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. [6,7].

2.2. The calculation of thermal conductivity for pure solids

2.2.1. 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 help of electron lifetime $\tau (l_{el} = v_F \tau)$:

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

With help of Drude theory [3] we can express thermal conductivity as the function of electrical conductivity σ :

$$\lambda_{el} = \sigma L T, \tag{10}$$

where L is temperature dependent constant.

2.2.2. Photon contribution to the thermal conductivity

It is more difficult to determine the thermal conductivity when there are nonfree electrons. Solids which obey this rule we called nonmetallic 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:

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

2.2.3. 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 :

$$\sigma_e = \frac{n_e^2}{m_b} \langle \tau(\epsilon, \vec{k}) \rangle. \tag{12}$$

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 $\langle \dots \rangle$ describe an average over all electron states. We can

also describe the electronic part of thermal conductivity with help of Eq. (12):

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

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 $\alpha_{\text{tr}}^2 F(\omega)$. A detailed theoretical expression is possibly to find in the work of Grimwall [9]. The Eliashberg coupling function allows us to write the thermal conductivity in the next expression:

$$\frac{1}{\lambda_{\text{el}}} = \frac{(4\pi)^2}{L_0 T \omega_{\text{pl}}^2} \int_0^{\omega_{\text{max}}} \frac{\hbar\omega/k_{\text{B}}T}{[\exp(\hbar\omega/k_{\text{B}}T - 1)][1 - \exp(-\hbar\omega/k_{\text{B}}T)]} \times \left\{ \left[1 - \frac{1}{2\pi^2} \left(\frac{\hbar\omega}{k_{\text{B}}T} \right)^2 \right] \alpha_{\text{tr}}^2 F(\omega) + \frac{3}{2\pi^2} \left(\frac{\hbar\omega}{k_{\text{B}}T} \right)^2 \alpha_{\text{tr}}^2 F(\omega) \right\} d\omega. \quad (14)$$

We can describe the phonons by an Einstein model:

$$\alpha_{\text{tr}}^2 F(\omega) = A\delta(\omega - \omega_{\text{E}}), \quad (15)$$

$$\alpha^2 F(\omega) = B\delta(\omega - \omega_{\text{E}}). \quad (16)$$

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

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

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:

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

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

2.2.4. 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 $F(\omega)$ [9]:

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

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:

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

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 $\tau(1)$:

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

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

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:

$$\lambda_{\text{ph}} = \lambda_0 \exp\left(-\frac{\theta_{\text{D}}}{T}\right), \quad (23)$$

where λ_0 is the constant.

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

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

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:

$$\theta_{\text{E}} = (0.72..0.75)\theta_{\text{D}}. \quad (25)$$

2.3. The calculation of thermal conductivity for nanoparticles [11–23]

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 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 [11–14]:

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

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,

$$n = \frac{3}{\psi}, \quad (27)$$

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:

$$\alpha = \frac{V_p}{V_0 + V_p} = n \frac{\pi}{6} d_p^3, \quad (28)$$

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 [15]:

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

Comparison between Eqs. (26) and (29) shows that Wasp model is a special case with the sphericity of 1.0 of the Hamilton and Crosser model. From the literature [13–15] we can find some other models (Maxwell, Jeffrey, Davis, Lu-Lin) with almost identical analytical results.

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 [16], 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 model (X) is expressed with the next equation:

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

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

We assume that the complex nanoparticle is composed of an elliptical nanoparticle with thermal conductivity λ_2 with half radii 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 [21] 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:

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

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:

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

3. Calculation of viscosity

3.1. Calculation of viscosity for pure fluid

In the presented paper will be presented Chung–Lee–Starling model (CLS) [6,7]. Equations for the viscosity and 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 , dimensionless dipole moment μ_r and an 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 viscosity in our model is obtained analytically [8] with the exception of correction factor:

$$\eta_0(T) = 26.69579 \cdot 10^{-1} \frac{\sqrt{MT}}{\Omega^{(2,2)} * \sigma^2} F_c, \quad (34)$$

where η is in Pa s, M is the molecular mass in g mol^{-1} , T is in K, $\Omega^{(2,2)}$ is a collision integral and σ is the Lennard-Jones parameter. The factor F_c has been empirically found to be [6,7]:

$$F_c = 1 - 0.2756\omega + 0.059035\mu_r^4 + \kappa, \quad (35)$$

where ω is the acentric factor, μ_r relative dipole moment and κ is a correction factor for hydrogen-bonding effect of associating substances such as alcohols, ethers, acids and water. For dense fluids Eq. (34) is extended to account for the effects of temperature and pressure by developing an empirically correlated function of density and temperature as shown below:

$$\eta = \eta_k + \eta_p, \quad (36)$$

$$\eta_k = \eta_0 \left(\frac{1}{G_2} + A_6 Y \right), \quad (37)$$

$$\eta_p = \left[36.344 \cdot 10^{-6} - (MT_c)^{0.5} / V_c^{2/3} t \right] A_7 Y^2 \times G_2 \exp(A_8 + A_9/T^* + A_{10}/T^{*2}), \quad (38)$$

$$Y = \rho V_c / 6, \quad G_1 = \frac{1.0 - 0.5Y}{(1.0 - Y)^3}, \quad (39)$$

$$T_c = \frac{1.2593\varepsilon}{k}, \quad V_c = (0.809\sigma(\dot{A}))^3, \quad (40)$$

$$G_2 = \frac{\{A_1(1 - \exp(-A_4 Y)) + A_2 G_1 \exp(A_5 Y) + A_3 G_1\}}{(A_1 A_4 + A_2 + A_3)}. \quad (41)$$

The constants A_1 – A_{10} are linear functions of acentric factor, reduced dipole moment and the association factor

$$A_i = a_0(i) + a_1(i)\omega + a_2(i)\mu_r^4 + a_3(i)\kappa, \quad \text{with } i = 1, 10, \quad (42)$$

where the coefficients a_0 , a_1 , a_2 and a_3 are presented in the work of Xuan and Roetzel [14].

3.2. The calculation of effective viscosity for nanofluids

It is well known that the earliest theoretical work on the effective viscosity was due to Einstein whose derivation led to the effective viscosity to be linearly related to the particle concentration [17]:

$$\eta_r = 1 + 2.5\alpha, \quad (43)$$

where η_r is the relative viscosity defined as the ratio of the effective viscosity of the particle fluid-mixture to the viscosity of the fluid and α is the volumetric concentration of the particles. Eq. (43) is applicable to suspensions with low-particle concentrations (less than 2%). With help of exponential model we can obtain the Cheng–Law [19] expression for the relative viscosity:

$$\eta_r = 1 + 2.5\alpha + \left(\frac{35}{8} + \frac{5}{4}\beta \right) \alpha^2 + \left(\frac{105}{16} + \frac{35}{8}\beta + \frac{5}{12}\beta^2 \right) \alpha^3 + \left(\frac{1155}{128} + \frac{935}{96}\beta + \frac{235}{96}\beta^2 + \frac{5}{48}\beta^3 \right) \alpha^4 + \dots, \quad (44)$$

where β is called the exponent. If we choose $\beta = 2$, we obtain the result is very close to the result obtained by Ward (W), who suggested the following expression for spherical particles:

$$\eta_r = 1 + (2.5\alpha) + (2.5\alpha)^2 + (2.5\alpha)^3 + (2.5\alpha)^4 + \dots. \quad (45)$$

The presented equation is fitted with the experimental data for the concentration up to 35%.

The viscosity 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 viscosity of nanofluids. The presented paper is the attempt how to calculate thermal conductivity of nanofluid analytically. Cheng and Law [19] developed the model for the effective thermal conductivity of two-component mixtures as a function of the viscosity of the pure fluid and the composition of particles and exponent factor.

The Cheng and Law or Ward models give very good results for two-phase flow with particles larger than 100 nm. For smaller particles the presented theory give wrong results with the deviation more than 100% in comparison with experimental results. The presented theoretical models for the calculation of the viscosity for nanofluids are only dependent on the viscosity of the liquid and their relative volume fraction, but not on particle size and the interaction between particles and the fluid.

In convection heat transfer in nanofluids not only on the thermal conductivity but also on the other properties such as specific heat, dynamic viscosity, etc., are important for analytical prediction. We can mention the factors discussed in the literature [17–27] as possible mechanisms for the anomalous enhancement of viscosity: the motion of nanoparticle, molecular level layering of the liquid at the liquid-particle interface and ballistic phenomena in nanoparticles, the effects of clustering in nanoparticles.

As in the case of analytical calculation of thermal conductivity, for the calculation of viscosity of nanofluids we have made the hypothesis that the most important additional contribution is liquid layering. With help of Eq. (43) we can express the renewed Ward model (RW):

$$\eta_r = 1 + (2.5\alpha_e) + (2.5\alpha_e)^2 + (2.5\alpha_e)^3 + (2.5\alpha_e)^4 + \dots. \quad (46)$$

Figs. 2 and 3 show the comparison between experimental results for the mixture water + TiO_2 , water + Al_2O_3 and analytical results. The mean diameter of TiO_2 particles is 27 nm and Al_2O_3 particles is 13 nm. The deviation of results between W (Eq. (45)) and RW model Eq. (46) and experimental results is extremely high. The renewed Ward model (RW) gives excellent results.

4. The calculation of thermodynamic properties for pure fluid

To calculate thermodynamic functions of state we applied the canonical partition [24,25]. Utilising the semi-classical formulation for the purpose of the canonical

ensemble for the N indistinguishable molecules the partition function Z can be expressed as follows [2]:

$$Z = \frac{1}{N!h^{3Nf}} \int \cdots \int \exp\left(-\frac{H}{kT}\right) \cdot d\vec{r}_1 d\vec{r}_2 \cdots d\vec{r}_N d\vec{p}_1 d\vec{p}_2 \cdots d\vec{p}_N, \quad (47)$$

where f stands for the number of degrees of freedom of individual molecule, H designates the Hamiltonian molecule system, vectors $\vec{r}_1, \vec{r}_2 \cdots \vec{r}_N \cdots$ describe the positions of N molecules and $\vec{p}_1, \vec{p}_2 \cdots \vec{p}_N$ momenta, k is Boltzmann's constant and h is Planck's constant. The canonical ensemble of partition function for the system of N molecules can be expressed like this:

$$Z = Z_0 Z_{\text{trans}} Z_{\text{vib}} Z_{\text{rot}} Z_{\text{ir}} Z_{\text{el}} Z_{\text{nuc}} Z_{\text{conf}}. \quad (48)$$

Thus the partition function Z is a product of terms of the ground state (0), the translation (trans), the vibration (vib), the rotation (rot), the internal rotation (ir), the influence of electrons excitation (el), the influence of nuclei excitation (nuc) and the influence of the intermolecular potential energy (conf).

Utilising the canonical theory for computing the thermodynamic functions of the state can be put as follows [5,6]:

$$\begin{aligned} \text{Pressure } p &= kT \left(\frac{\partial \ln Z}{\partial V} \right)_T, \\ \text{Internal energy } U &= kT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_V, \\ \text{Free energy } A &= -kT \cdot \ln Z, \\ \text{Entropy } S &= k \left[\ln Z + T \left(\frac{\partial \ln Z}{\partial T} \right)_V \right], \\ \text{Free enthalpy } G &= -kT \left[\ln Z - V \left(\frac{\partial \ln Z}{\partial T} \right)_V \right], \\ \text{Enthalpy } H &= kT \left[T \left(\frac{\partial \ln Z}{\partial T} \right)_V + V \left(\frac{\partial \ln Z}{\partial V} \right)_T \right], \end{aligned} \quad (49)$$

where T is temperature and V is volume of molecular system. The computation of the individual terms of the partition function and their derivatives except of the configurational integral is dealt with in the works of Lucas [24].

4.1. Revised Cotterman model (CYJ) [26]

Revisited Cotterman EOS is based on the hard sphere perturbation theory. The average relative deviation for pressure and internal energy in comparison with Monte-Carlo simulations are 2.17% and 2.62% respectively for 368 data points [9]. The configurational free energy is given by:

$$A_{\text{conf}} = A^{\text{hs}} + A^{\text{pert}}, \quad (50)$$

$$\frac{A^{\text{hs}}}{R_m T} = \frac{4\eta - 3\eta^2}{(1 - \eta)^2}, \quad (51)$$

$$A^{\text{pert}} = \frac{A^{(1)}}{T^*} + \frac{A^{(2)}}{T^{*2}}, \quad (52)$$

$$\frac{A^{(1)}}{R_m T} = \sum_{m=1}^4 A_{1m} \left(\frac{\eta}{\tau} \right)^m, \quad \frac{A^{(2)}}{R_m T} = \sum_{m=1}^4 A_{2m} \left(\frac{\eta}{\tau} \right)^m, \quad (53)$$

$$\tau = 0.7405, \quad \eta = \frac{\pi \rho D^3}{6}, \quad (54)$$

where η is packing factor, D is hard-sphere diameter.

With help of configurational free energy we can calculate all configurational thermodynamic properties. Expressions for calculation of configurational entropy and internal energy are shown in literature [9]. We carried out all other expressions for calculation of thermophysical properties.

5. The calculation of thermodynamic properties for pure solids

Our thermodynamic system consists of N particles associated by attractive forces. Atoms in a crystal lattice are not motionless but they constantly thermally oscillate around their positions of equilibrium. At temperatures far below the melting point the motion of atoms is approximately harmonic [4,9]. This assembly of atoms has $3N - 6$ vibration degrees of freedom. Ignore 6 vibration degrees of freedom and mark the number of vibration degrees of freedom with $3N$.

Through the knowledge of independent harmonic oscillators the distribution function Z can be derived as follows:

$$Z = \left[\frac{\exp\left(-\frac{hv}{2k_B T}\right)}{1 - \exp\left(-\frac{hv}{k_B T}\right)} \right]^{3N}. \quad (55)$$

In Eq. (20) ν is the oscillation frequency of the crystal. The term hv/k is the Einstein temperature.

In comparing the experimental data for simple crystals a relatively good matching with analytical calculations at higher temperatures is observed whereas at lower temperatures the discrepancies are higher. This is why Debye corrected the Einstein's model by taking account of the interactions between a number of quantized oscillators. The Debye approximation treats a solid as an isotropic elastic substance. Using the canonical distribution the partition function [11] may be written as:

$$\begin{aligned} \ln Z &= -\frac{9}{8} N \frac{\theta_D}{T} - 3N \cdot \ln \left(1 - \exp\left(-\frac{\theta_D}{T}\right) \right) \\ &+ 3N \frac{T^3}{\theta_D^3} \int_0^{\theta_D/T} \frac{\xi^3}{\exp(\xi) - 1} d\xi. \end{aligned} \quad (56)$$

In Eq. (52) θ_D is the Debye temperature: $\theta_D = \frac{\nu_{\text{max}} h}{k}$. By developing the third term in Eq. (56) into a series for a higher temperature range [2] we can write:

$$\frac{\xi^3}{\exp(\xi) - 1} = \xi^2 - \frac{1}{2} \xi^3 + \frac{1}{12} \xi^4 - \frac{1}{720} \xi^6 + \cdots \quad (57)$$

Using Eq. (53) and (52) turns into the following expression:

$$\ln Z = -\frac{9}{8}N\frac{\theta_D}{T} - 3N \cdot \ln\left(1 - \exp\left(-\frac{\theta_D}{T}\right)\right) + 3N\left(\frac{T}{\theta_D}\right)^3 \left[\frac{1}{3}\left(\frac{\theta_D}{T}\right)^3 - \frac{1}{8}\left(\frac{\theta_D}{T}\right)^4 + \frac{1}{60}\left(\frac{\theta_D}{T}\right)^5 - \frac{1}{5040}\left(\frac{\theta_D}{T}\right)^7 + \frac{1}{272160}\left(\frac{\theta_D}{T}\right)^9 - \dots\right]. \quad (58)$$

The relation between the Einstein and Debye temperature may be written as [12–15]:

$$\theta_E = (0.72 \dots 0.75)\theta_D. \quad (59)$$

The Debye characteristic temperature was determined by means of the Grüneisen independent constant γ :

$$\theta = CV^{-\gamma}, \quad (60)$$

where C is constant dependent on material.

We developed a mathematical model for the calculation of thermodynamic properties of polyatomic crystals. The derivations of the Einstein and Debye equations, outlined in the previous paragraphs, apply specifically to monoatomic solids, i.e., those belonging to the cubic system. However, experiments have shown that the Debye equation represents the values of specific heat and other thermophysical properties for certain other monoatomic solids, such as zinc, which crystallizes in the hexagonal system. Suppose that the crystal contains N molecules, each composed of s atoms. Since there are Ns atoms, the crystal as a whole has $3Ns$ vibrational modes. A reasonable approximation is obtained by classifying the vibration into:

- $3N$ lattice vibrations, which are the normal modes discussed in the Debye treatment (acoustical modes).
- Independent vibrations of individual molecules in which bond angles and lengths may vary. There must be $3N(s-1)$ of these (optical modes). We expressed the optical modes using the Einstein model.

5.1. Electronic gas in metals

We are interested in electrons capable of moving in a crystal and not belonging to any individual atoms but entirely to the crystal. Such are, for example, conduction electrons in metals. A number of such electrons may be called electronic gas. Using the Fermi–Dirac statistics the configuration integral [4] may then be calculated for temperatures lower than the Fermi temperature:

$$T_F = \frac{\varepsilon_F}{k_B}. \quad (61)$$

For metals the Fermi temperature is a few thousand Kelvins. In Eq. (26) ε_F is Fermi energy.

$$A_{cl} = \frac{3}{5}N\varepsilon_F \left(1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{\varepsilon_F}\right)^2\right) - Nk_B \frac{\pi^2}{2} \frac{k_B T^2}{\varepsilon_F}. \quad (62)$$

The analytical calculation of configuration integral in solids is a very difficult task. Most frequently numerical procedures are applied in practical computations by means of the Monte-Carlo method [11]. Nevertheless, the presented method requires a lot of computer time with another serious drawback being also that it does not provide a functional dependence of thermodynamic properties on temperature and volume. Empirical equations [6] are frequently used as well, though mostly without any theoretical basis built on a molecular view of the world. In the paper presented we used the perturbation VDW theory for solids around the model of hard spheres [4] to calculate the thermodynamic properties of state. In order to calculate the mixtures of atoms of hard spheres we obtain the configuration free energy for a certain binary crystal:

$$A_{\text{conf}0} = Nk_B T \times \left(-3 \ln \left(\frac{V^* - 1}{V^*}\right) + 5.124 \cdot \ln V^* - 20.78V^* + 9.52V^{*2} - 1.98V^{*3} + C_0 + \psi_1 \cdot \ln \psi_1 + \psi_2 \cdot \ln \psi_2\right), \quad (63)$$

$$C_0 = 15.022, \quad V^* = \frac{V}{V_0}, \quad V_0 = \frac{N\sigma^3}{\sqrt{2}}.$$

In case of a crystal formed of atoms of the same type free energy can be written as:

$$A_{\text{conf}0} = Nk_B T \left(-3 \ln \left(\frac{V^* - 1}{V^*}\right) + 5.124 \cdot \ln V^* - 20.78V^* + 9.52V^{*2} - 1.98V^{*3} + C_0\right). \quad (64)$$

To calculate the perturbation contribution the VDW model was used. In most of the technical literature [4] the VDW model is treated only in relation to atomic structure, whereas we additionally presented the temperature-dependent coefficients.

$$A_{\text{conf}1} = -\frac{a(\psi_1, \psi_2, T)}{V}. \quad (65)$$

The configuration integral is thus formed by the contribution of hard spheres and perturbation:

$$A_{\text{conf}} = A_{\text{conf}0} + A_{\text{conf}1}. \quad (66)$$

In our case coefficient a was determined as a temperature-dependent polynome following a comparison between experimental data and analytical results:

$$a = a_0 + a_1 T + a_2 T^2. \quad (67)$$

Coefficients a_0 , a_1 , a_2 are obtained by numerical approximation and the comparison with thermodynamic data.

6. Thermodynamic properties for nanofluids

The third main parameter involved in calculating heat transfer rate of the nanofluid is heat capacity. For the

synthesized nanoparticle-fluid suspension we can predict the thermodynamic properties with the next expression:

$$(\rho c_p)_{nf} = (1 - \phi)(\rho c_p)_f + \phi(\rho c_p)_p, \quad (68)$$

where ρ is a density of nanofluid:

$$\rho = (1 - \phi)\rho_f + \phi\rho_p. \quad (69)$$

6.1. Results and comparison with experimental data

In the present paper, we will show analytical computations for the mixture between copper nanoparticles, aluminium oxide nanoparticles and ethylene glycol. 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 aluminium oxides. In our case we have used experimental results from the literature [15] where copper average nanoparticles diameter are smaller than 10 nm. For Al₂O₃ nanoparticles authors Eastman et al. reported [15] that the average diameter is 35 nm.

Figs. 1, 2 and 5 show the comparison between analytical data and experimental data [2,27] for pure substances. Fig. 3 shows the comparison between analytical calculation (CLS model) and results obtained by fluid properties calculator (FPC). FPC model is installed on the internet <http://www.mhlt.uwaterloo.ca/old/onlinetools/airprop/airprop.html>. We have compared for copper our analytical results

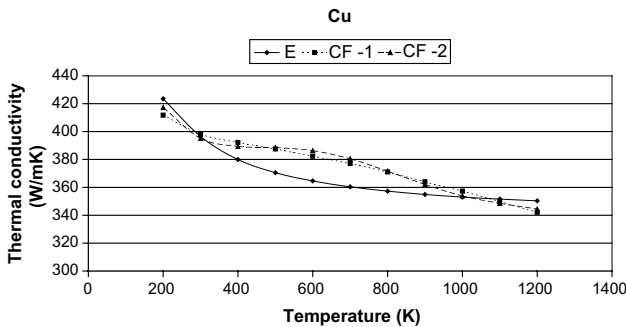


Fig. 1. Thermal conductivity for copper.

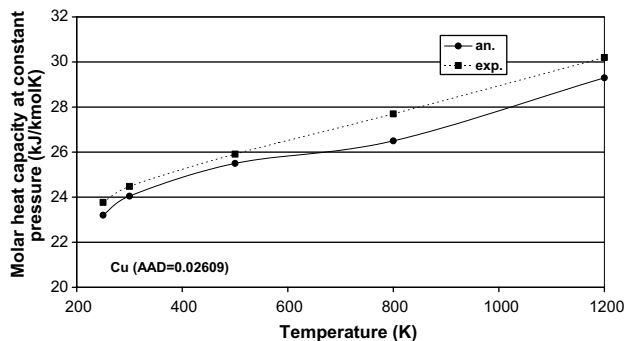


Fig. 2. Isobaric molar heat for copper.

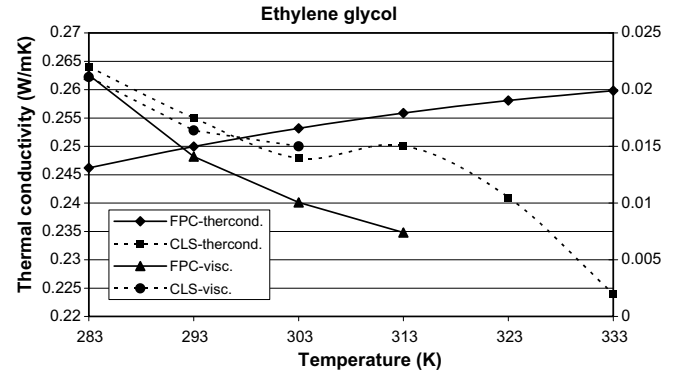


Fig. 3. Viscosity and thermal conductivity of ethylene glycol.

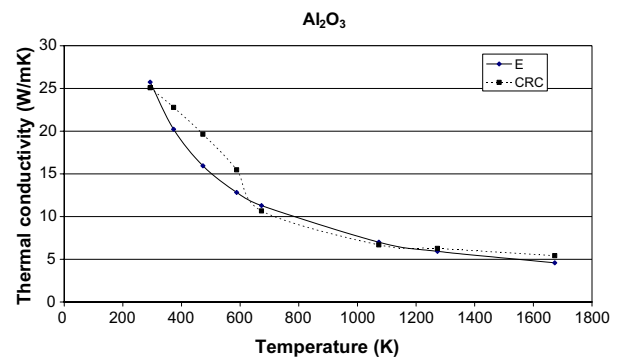


Fig. 4. Thermal conductivity of aluminium oxide.

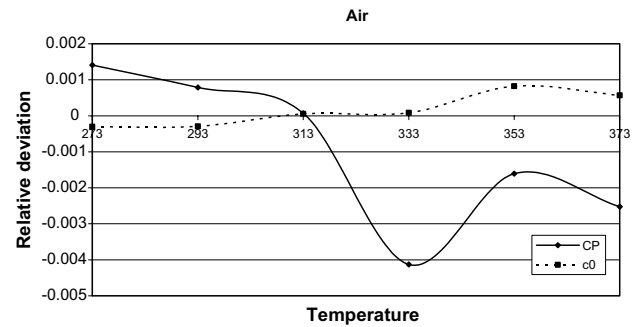


Fig. 5. Relative deviation of velocity of sound and isobaric molar heat for air between CYJ model and REFPROP 7.1 model.

also with experimental data and comparison shows relatively good agreement. Fig. 5 shows the comparison between analytical calculation (CYJ model) and REFPROP 7.1 model for air [28] (see Fig. 4).

The comparison shows very good agreement. Figs. 6 and 7 show the analytical calculation of mixture between ethylene glycol and copper and aluminium oxide (Al₂O₃) nanoparticles for thermal conductivity ratio. The results for thermal conductivity obtained by X and RHC model show relatively very good agreement in comparison with experimental results. Thermal conductivity predicted by HC model give much lower values as experimental results. Figs. 8 and 9 show the comparison between experimental results for the mixture water + TiO₂, water + Al₂O₃ and

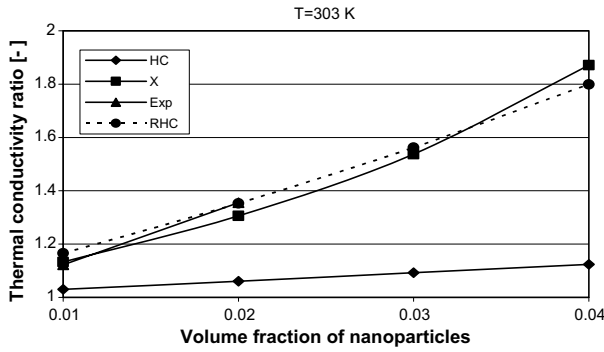


Fig. 6. Thermal conductivity of mixture copper nanoparticles + ethylene glycol at various composition at 303 K.

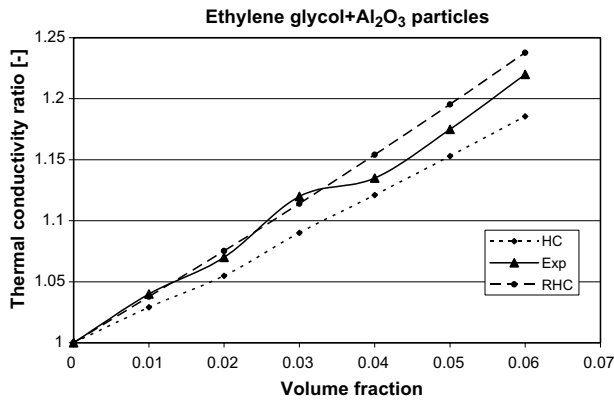


Fig. 7. Thermal conductivity for Al₂O₃ nanoparticles + ethylene glycol.

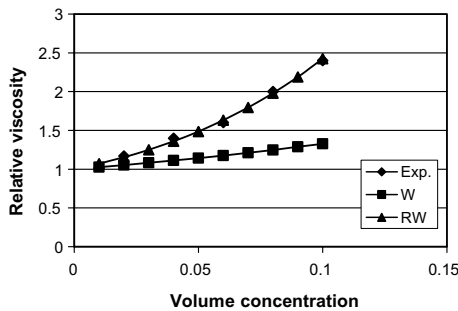


Fig. 8. Relative viscosity for the mixture water + TiO₂ nanoparticles for the shear rate 384 s⁻¹.

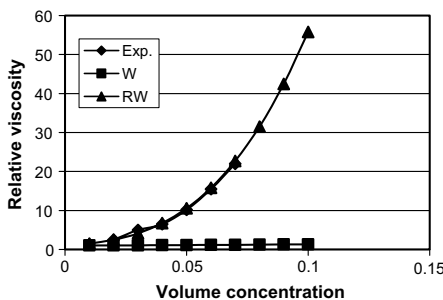


Fig. 9. Relative viscosity for the mixture water + Al₂O₃ nanoparticles for the shear rate 115.2 s⁻¹.

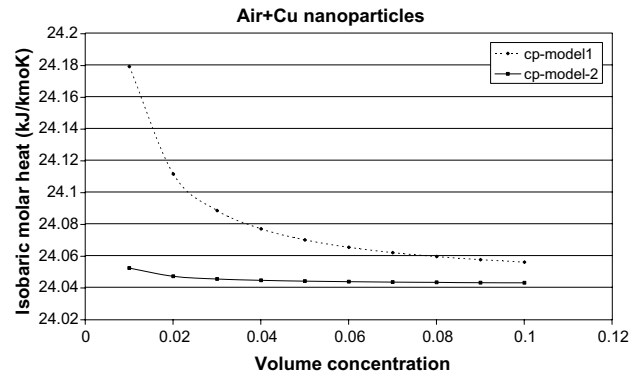


Fig. 10. Thermodynamic properties for Cu nanoparticles + air.

analytical results. The mean diameter of TiO₂ particles is 27 nm and Al₂O₃ particles is 13 nm. The deviation of results between W (Eq. (45)) and RW model (Eq. (46)) and experimental results is extremely high. The renewed Ward model (RW) gives excellent results. Fig. 10 shows the calculation for isobaric molar heat for copper nanoparticles + air. Fig. 10 shows that for equilibrium thermomechanical properties of state is almost no enhancement with variation of volume concentration of nanoparticles. Model 1 is based on fundamental Eq. (69) and model 2 in Fig. 10 is based on Eq. (69) and improved with Eq. (32). Both models show almost the same analytical results.

7. Conclusion and summary

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

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