Application of Perturbed Hard-Sphere Equation of State to the Study of Volumetric Properties of Nano-Fluids

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Abstract

This paper aimed to examine the application of a perturbed hard-sphere (PHS) scheme for modeling the volumetric properties of nanofluids. In this regard, PHS scheme has been employed to develop an analytical equation of state (EOS) to correlate and predict the volumetric properties of some nanofluids containing SnO_2 , ZnO , Co_3O_4 , TiO_2 -anatase (-A), TiO_2 -rutile (-R), CuO and Al_2O_3 as nanoparticles dispersed in ethylene glycol, poly ethylene glycol, water, poly ethylene glycol+water and ethylene glycol+water as base fluids. Two temperature-dependent parameters appeared in the EOS were expressed in terms of molecular scaling constants σ , the effective hard-sphere diameter, and ε , the non-bonded interaction energy. The aforementioned scaling constants were correlated with melting temperatures and true densities which demonstrated the rationality of these constants. The performance of the proposed model was assessed by predicting 1348 density data, for which their measured values were available in the literature over the pressure range from 0.1 to 45 MPa and temperature range from 273 to 363 K. The overall average absolute deviation (AAD) of the correlated (at 0.1 MPa) and predicted (at elevated pressures) densities of 9 studied nanofluids from the experimental data was found to be 0.44%. Generally, this work showed that PHS is an appropriate scheme for the correlation and prediction of the properties of this class of fluids by the help of crossed interaction parameters between nanoparticles and base fluid molecules. The isothermal compressibility coefficients and excess volumes of studied nanofluids have also been investigated by the proposed model.

Keywords: Nanofluid; Equation of state, thermodynamic properties

1. Introduction

A nanofluid is defined as a dilute suspension of nanometer-size particles and fibers dispersed in a liquid. Some nanofluids are suspensions of metallic nanoparticles in conventional base fluids (denoted as nanoparticle/base fluid) [1]. As a result, when compared to the base fluid, changes in physical properties of such mixtures occur, e.g., viscosity and thermal conductivity. Recently, they came into focus as alternative heat transfer fluids flow [2-6]. Besides thermal conductivities which is crucial for use in the heat transferring phenomena, other thermophysical properties such as density is as critical as thermal conductivities in engineering systems [7]. In order to evaluate the fluid dynamic and heat transfer performances of nanofluids in thermal cycles, the density must be known accurately to compute matter and energy balances [8]. Since the density data are scarce for nanofluids, specifically those reported at the elevated pressures, the development of empirical and semi-theoretical models such as $P\rho T$ correlations and equations of state (EOSs) to supplement the available experimental data seems is useful.

Although the great efforts devoted to study the transport properties of nanofluids through empirical, semi-empirical, theoretical and molecular simulation methods [9-17], less emphasis has been placed on presenting analytical models for volumetric data of nanofluids. We briefly review the previous approaches within the calculation of volumetric data of nanofluids from the most widely used Tammann-Tait equation to those are related to computer-aided genetic algorithms as follows:

The densities of nanofluids and nanomaterial have been correlated based on the several EOSs and $P\rho T$ correlations. The most widely used one is Tammann-Tait equation [18-20] and that was adopted for nanometer sized particles by Sharma-Kumar [21] and Pak-Cho [22]. Sharma and Kumar developed an EOS for nanomaterials as follows:

$$P = a_1 \left(1 - \frac{V}{V_0}\right) + a_2 \left(1 - \frac{V}{V_0}\right)^2 \quad (1)$$

where, P is the pressure, V/V_0 the relative change in volumes and 0 refers to their initial condition. a_1 and a_2 are the size-dependent parameters, which have been proposed to be determined from the definition of bulk modulus and its first order pressure derivative [21]. Very Recently, Sugata and Piri [23] employed a perturbed-chain statistical associating fluid theory (PC-SAFT) coupled with Young–Laplace equation [24] to investigate and represent fluid-phase equilibria in nanosize pores. Pak and Cho [22] presented the general equation for representing the density of nanofluids as follows:

$$\rho_{nf} = \rho_{np}\varphi + \rho_{bf}(1 - \varphi) \quad (2)$$

where, ρ_{nf} is the density of the nanofluid, ρ_{np} is the density of the particle, φ is the particle volume concentration, and ρ_{bf} is the base fluid density. Vajjha et al. [25] employed Pak-Cho equation to calculate the nanofluid densities; the need for true values of base fluid and nanoparticle densities limits the applicability of the Pak-Cho equation.

The artificial neural network method has also been employed to correlate and predict $P\rho T$ data of nanofluids. Karimi and Yousefi [26] correlated the experimental density of four nanofluids in the temperature range of 273–323 K and the nanoparticle volume fraction up to 10% with average absolute deviation (AAD) equal to 0.13% using neural network approach. It should be mentioned that these methods need large datasets for training.

Several researchers tried to correlate high-pressure volumetric data of nanofluids based on Tammann-Tait equation [16, 17]. Although the Tammann-Tait equation leads to the quit accurate results for the density correlation of nanofluids, however, in the case of nanofluids the applicability of that equation is limited to the

fitting of numerous coefficients to each nanoparticle concentration. This issue limits the use of Tammann-Tait equation for the practical purposes. It should be added that Tammann-Tait equation doesn't make significant contributions to understand the molecular interactions operating between nanoparticle surface and base fluid molecules.

By employing molecular-based EOS, one can both predict accurately the $P\rho T$ data of nanofluids and investigate the effect of molecular interactions on their volumetric behavior using the crossed interaction terms. Using a perturbed hard sphere (PHS) equation of state is a proper route to achieve this goal. The PHS EOS is based on the molecular theories of statistical mechanics[27], in which the reference physical model serves as the hard-sphere repulsion and a perturbation part denotes the dispersion forces. Likewise, PHS EOS belongs to a long history and comprehensive theoretical backgrounds among the literature [28-30]. Numerous researchers[29, 31-34] brought PHS EOS in focus over the past 2 decades and consequently, the performance of such model has been well-established for various classes of liquids[28, 35-42].

In the present work, for the first time, we examine the applicability of a perturbed hard-sphere scheme to correlate and predict the volumetric properties of nanofluids. As mentioned above, it was found that, regardless of the fact that the PHS scheme had to be extended by orders of magnitude, it was still an appropriate scheme to model the properties of highly non-simple fluids by the help of crossed interaction parameters between nanoparticles and base fluid molecules; this fact is attributed to its theoretical basis. Also, we show that our PHS model yields nanoparticle parameters that correlate regularly with the melting temperatures and true densities of compacted nanopowder.

2. Theory

2.1. Equation of state for pure base fluid

In the framework of the perturbation theory of liquids [27], the compression factor of a dense fluid comprises hard-sphere contributions and dispersion forces. According to the perturbation theory, the general frame of the PHS EOS of interest is that of Carnahan-Starling-van der Waals equation which was proposed by Song et al. [28, 43], *viz*;

$$Z = \frac{P}{\rho k_B T} = 1 + b(T) \rho g(\sigma^+) - \frac{a(T) \rho}{k_B T}, \quad (3)$$

Where Z is the compression factor, P is the pressure, ρ is the number (molar) density and $k_B T$ is the thermal energy per molecule. $a(T)$ and $b(T)$ parameters represent respectively, attractive forces between the pairs of hard-sphere and the van der Waals co-volume. $g(\sigma^+)$ denotes the radial distribution function (RDF) of hard-spheres at contact developed by Carnahan-Starling [44], which reads as:

$$g(\sigma^+) = \frac{1 - \eta/2}{(1 - \eta)^3}, \quad (4)$$

Here η is packing fraction of hard-sphere fluid defined as:

$$\eta = \frac{b(T) \rho}{4}, \quad (5)$$

Eq. (3) has two parts; 1) the Carnahan–Starling expression [44] taken as physical reference hard-sphere model and 2) van der Waals (vdW) attraction term to represent dispersion forces. Two temperature-dependent parameters of Eq. (3) i. e. the strength of attractive forces between two spheres $a(T)$ and the molecular size, $b(T)$ are theoretically related to the pair-potential function and temperature. Until now several approaches have been proposed to evaluate these parameters. Generally, one may perform the integral equations derived by Song and Mason [32, 43, 45] which require the pair potential energy function of physical systems of interest. However, the pair-

potential function is seldom accurately known for most physical systems especially for inhomogeneous mixtures such as nanofluids, in which the interaction between the nanoparticles and the base fluid are due to a combination of factors such as ionic double repulsive layer in the nanoparticle surface and also nanoparticle size [46]. In this respect, the determination of these parameters through the integral equations is not straightforward. The temperature-dependent parameters, $a(T)$ and $b(T)$, can be expressed in terms of suitable reducing constants. They are universal function of the reduced temperature. In the following, we show how to express two temperature-dependent parameters appeared in the PHS EOS, using the universal functions of reduced temperature, T_r , in terms of molecular scaling constants σ , the effective hard-sphere diameter, and ε , the non-bonded interaction energy and in corresponding states form as:

$$a(T) = \frac{2\pi}{3} \sigma^3 \varepsilon F_a(k_B T / \varepsilon) \quad (6)$$

$$b(T) = \frac{2\pi}{3} \sigma^3 F_b(k_B T / \varepsilon) \quad (7)$$

Where, ε is the dispersive energy parameter and σ denotes the hard-core diameter. Further, F_a and F_b are the universal functions of the reduced temperature, $k_B T / \varepsilon$ which can be written as the following empirical formula[47, 48]:

$$F_a(k_B T / \varepsilon) = a_1 \exp\left(-a_2 \frac{k_B T}{\varepsilon}\right) + a_3 \exp\left[-a_4 \left(\frac{k_B T}{\varepsilon}\right)^{3/2}\right] \quad (8)$$

$$F_b(k_B T / \varepsilon) = b_1 \exp\left(-b_2 \frac{k_B T}{\varepsilon}\right) + b_3 \exp\left[-b_4 \left(\frac{k_B T}{\varepsilon}\right)^{3/2}\right] \quad (9)$$

where;

$$\begin{aligned} a_1 &= 1.058393, & b_1 &= 0.798019 \\ a_2 &= -0.879380, & b_2 &= 0.908086 \\ a_3 &= 0.609445, & b_3 &= 0.521304 \end{aligned}$$

$$a_4 = -0.314038, \quad b_4 = -0.407266$$

2.2. Extension of the PHS EOS to nanofluids

The mixture version of the PHS EOS can be summarized as follows:

$$Z^{HS} = 1 + \rho \sum_i \sum_j x_i x_j b(T)_{ij} (g(\sigma^+)_{ij}) \quad (10)$$

where, $g(\sigma^+)_{ij}$ represents the pair radial distribution function of hard-sphere mixtures at contact which has been taken from the Boublik–Mansoori–Carnahan–Starling (BMCS) equation [49, 50]. x_i and x_j are mole fractions of components i and j , respectively, and the summations run over all the components.

The required dispersion term for representing the attraction forces is that of vdW equation together with the vdW one fluid mixing rule as:

$$Z^{disp.} = - \frac{\rho}{k_B T} \sum_i \sum_j x_i x_j a_{ij} \quad (11)$$

In the case of hard-sphere mixture, the interaction diameters of unlike hard-spheres are considered to be additive; therefore, b_{ij} can be expressed as:

$$b_{ij} = \frac{1}{8} \left(b(T)_i^{1/3} + b(T)_j^{1/3} \right)^3 \quad (12)$$

The attractive forces between two hard-sphere species of mixture including i and j components can be written as follows:

$$a_{ij} = \frac{2\pi}{3} \sigma_{ij}^3 \varepsilon_{ij} F_a \left(k_B T / \varepsilon \right)_{ij} (1 - k_{ij}) \quad (13)$$

In the present model a binary interaction parameter, k_{ij} is also added to crossed attractive parameter (i.e., Eq. (13)) for understanding the measure of interplay between nanoparticle surface-base fluid (k_{np-bf}) and base fluid-base fluid (k_{12}) molecules. The present method for calculating a and b can be extended to mixtures by

using a simple geometric mean and an arithmetic mean combining rules for the proposed microscopic scaling constants; i.e.,

$$(\varepsilon/k)_{ij} = \sqrt{(\varepsilon/k)_i (\varepsilon/k)_j} \quad (14)$$

$$\sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j) \quad (15)$$

$$F_a(kT/\varepsilon)_{ij} = \sqrt{F_a(kT/\varepsilon)_{ii} F_a(kT/\varepsilon)_{jj}} \quad (16)$$

$g^{\text{HS}}(\sigma^+)_{ij}$ represents the pair radial distribution function of hard-sphere mixtures at contact which has been taken from the BMCS equation[49, 50]:

$$\left(g(\sigma^+)\right)_{ij} = \frac{1}{1-\eta} + \frac{3 \xi_{ij}}{2 (1-\eta)^2} + \frac{\xi_{ij}^2}{2 (1-\eta)^3} \quad (17)$$

With

$$\xi_{ij} = \frac{\rho}{4} \left(\frac{b(T)_i b(T)_j}{b(T)_{ij}} \right)^{1/3} \sum_k^m x_k b_k^{2/3} \quad (18)$$

η is the packing fraction of hard-sphere mixture defined as:

$$\eta = \frac{\rho}{4} \sum_i^m x_i b(T)_i \quad (19)$$

3. Results and discussion

3.1. Parameter estimations

In order to apply the proposed PHS EOS to nanofluids, the values of molecular characteristics, ε and σ to be used in Eqs. (6)-(9) must be determined. These values were adjusted empirically from the $P\rho T$ data of base fluids of interest, for which their values were taken from literature [51-53]. To determine the above-mentioned parameters, the following objective function (*OBF*) was minimized for each base fluid using the least-squares method:

$$OBF = \min \frac{1}{n} \sum_{i=1}^n \frac{|\rho_i^{\text{Exp.}} - \rho_i^{\text{Calc.}}|}{\rho_i^{\text{Exp.}}} \quad (20)$$

Where n is the number of trained density data. Generally, from 204 literature data points [51-53] applied to 3base fluids of interest, the minimum value of OBF was found to be 0.0068. In the case of nanoparticles under consideration, the molecular parameters were optimized by true densities of compacted nanopowder[54] over the desired temperature range. To show the rationality of estimated molecular parameters of studied nanoparticles, Figure 1 has been presented. It depicts the correlations of the molecular parameters, ε and σ , with melting temperature, T_m and true density[54, 55]of studied nanoparticles, both of which were shown in **a** and **b** plots, respectively. The numerical values of these parameters havealso been listed in the Table 1.

3.2. Density estimations

In the first step, the proposed PHS EOS was assessed for binary base fluids including ethylene glycol (EG) +water and poly ethylene glycol (PEG) + water, which are widely used for cooling purposes. However, some binary interaction parameters should be taken into account to define the non-ideal volumetric behaviors in these binary systems. Table 2 shows the predicted results for studied binary base fluids together with binary interaction parameters, k_{12} to be used in crossed attraction parameter, a_{12} .The results were shown as the AAD (in %) of correlated (at 0.1 MPa) and predicted (at elevated pressures) densities using proposed PHS EOS from the experimental data [56-58].

Since the studied nanofluids comprised the suspended nanoparticles in pure and binary base fluids, Eqs. (10)-(19) should to be capable of describing the multi-component mixtures. Using double and triple combing rules one can extend the present equation of state to multi-component nanofluids.

We have examined the proposed PHS EOS by correlating (at 0.1 MPa) and predicting (at elevated pressures) the mass density of 9nanofluids having base-fluids containing ethylene glycol-, poly ethylene glycol-, water-, poly ethylene glycol+water- and ethylene glycol+water along with the dispersed nanoparticles including SnO₂, ZnO, Co₃O₄, TiO₂-anatase (-A), TiO₂-rutile (-R), CuO and Al₂O₃. Our computations were carried out over the temperature range from 273 K to 363 K and pressure range from 0.1 up to 45 MPa and comparing with the experimental data [25, 53, 56, 59-62]. Our results have been summarized in Table 2. In the present work, 1348experimental data points have been taken to check the reliability of our PHS EOS. For aforementioned data points, the mean AAD of the calculated densities from the literature values was found to be 0.44%. The numerical values of estimated binary interaction parameters for studied nanofluids have also been included in Table 2. It should be mentioned that the sign of parameters k_{np-bf} and k_{12} represents the repulsive and attractive molecular interactions between nanoparticle surface-base fluid (k_{np-bf}) and base fluid-base fluid (k_{12}) molecules, respectively. It should be added that the uncertainty of the predicted densities of all nanofluids studied in this work was of the order of $\pm 2.73\%$.

Figure 2 displays the linearity of the nanofluid densities versus pressure for typically SnO₂/EG (**a**-plot) and TiO₂-R/EG (**b**, **c**-plots) at several isotherms and nanoparticle mole fractions from 0.0136 to 0.039. The markers represent the experimental isotherms of Mariano et al. [53] and Cabaleiro et al. [59] and solid lines are those predicted using the proposed PHS EOS. As the figure illustrates, the linear regularity and some fairly smooth curves associated with isotherms of Mariano et al. [53] and Cabaleiro et al. [59] can be shown well by the present PHS model using the crossed interaction parameters.

3.3. Isothermal compressibility

The isothermal compressibility is related to the fluctuations in volume/density versus pressure. Using an EOS, one can easily estimate the isothermal compressibility through standard classical thermodynamic relation:

$$\kappa_T = - \left(\frac{1}{V} \right) \left(\frac{\partial P}{\partial V} \right)_T^{-1} = \frac{1}{\rho} \left(\frac{\partial P_{EOS}}{\partial \rho} \right)_T^{-1} = \frac{1}{\eta} \left(\frac{\partial P_{EOS}}{\partial \eta} \right)_T^{-1} \quad (21)$$

As indicated in Eqs. (21), this property is closely related to the derivative of the pressure with respect to density or packing fraction at constant temperature. In this section, the values of isothermal compressibility coefficients of some selected nanofluids were estimated through our proposed PHS EOS. Figure 3 is provided to show how the predicted isothermal compressibilities pass through the literature data points [56, 59]. Figure 3 illustrates three isothermal compressibility vs. pressure plots for TiO₂-R/EG at $x_{np}=0.0136$ (**a**-plot), TiO₂-R/EG at $x_{np}=0.039$ (**b**-plot) and ZnO/EG+water at $x_{np}=0.0183$ (**c**-plot). The solid lines are our predictions and markers are those reported by Cabaleiro et al. [56, 59], where employed Tammann-Tait equation for correlating the high-pressure volumetric behavior of nanofluids of interest. Figure 3 also demonstrates that the model predicts an almost linear behaviour of isothermal compressibility of the selected EG- and EG + water-based nanofluids against the pressure (as indicated in **a-c** plots) which reveals systematic predictions for isothermal compressibility over the whole pressure range. Instead, the literature data (markers) obtained from Tammann-Tait equation, don't show a regular trend for pressure dependency of κ_T especially for the case of (**b**)-plot. Although the isothermal compressibility are overestimated using the proposed PHS EOS, the trend of this property in terms of the pressure is well established by the present model over different nanoparticle mole fractions up to 0.039. The predicted values of this property have been tabulated as supplementary material to this manuscript.

The proposed PHS EOS has also been examined to predict the thermal expansion coefficients of nanofluid. Figure 4 shows the results of a typical calculation for thermal expansion coefficients of ZnO/EG+water at $x_{np}= 0.0183$ (**a**-plot) and $x_{np}= 0.0378$ (**b**-plot). The solid lines are our predictions and markers are the isotherms of Cabaleiro et al. [56] which have been obtained from Tammann-Tait type equation. Figure 4 revealed that the model didn't represent thermal expansion coefficients of studied nanofluids as accurate as isothermal compressibility and the calculated values were overestimated with relative deviations from the results of Tammann-Tait equation above 30%. This observation is attributed to the fact that the molecular parameters of the model were fixed through experimental density data rather than both density and derivative properties.

3.4. Excess molar volume

The molecular interactions in these systems are complex, and excess properties certainly provide valuable information about the intermolecular interactions. The excess volume, V^E is calculated from the following expression:

$$V^E = \frac{1}{\rho_{nf}} - \sum_{i=1}^n \frac{\varphi_i}{\rho_i} \quad (22)$$

where, φ stands for the mass fraction and n is the number of mixture components. ρ_{nf} and ρ_i are suspension and i^{th} compound densities, respectively. Typically, the excess volumetric behavior of three selected nanofluids including SnO₂/EG, Co₃O₄/EG and CuO/water were investigated using the PHS model. The outcomes of the computations are shown in Figure 5. The Figure 4 depicts three plots for isothermal excess volumes against nanoparticle mass fractions (in %), at atmospheric pressure as well as 10 MPa, from 1% to 5% concentrations. The solid lines are our predictions and markers are those reported by Pastoriza-Gallego et al.[62] and Mariano et al. [53, 61].

For the case of SnO_2/EG (**a**-plot), $\text{Co}_3\text{O}_4/\text{EG}$ (**b**-plot) the predicted results are fairly close to experimental data [53, 61, 62] but as the mass fractions increase the model fails to represent accurately the excess volumetric behaviors. In the case of CuO/water (**c**-plot), the predicted excess molar volumes did not coincide with those reported in literature. In accordance with Mariano et al. [53] arguments, this volumetric trend may be attributed to the interface effects on the bulk fluid properties produced by the solid nanoparticle surface, or even to the interactions among nanoparticles. The non-ideal behavior of nanofluids increases with the concentration of nanoparticles while reduce upon increasing the temperature. For the case of SnO_2/EG and $\text{Co}_3\text{O}_4/\text{EG}$ suspensions it was found that V^E values were less sensitive to temperature. This behavior can be attributed to the average particle size of nanoparticles.

4. Conclusion

In the present study for the first time a simple analytical equation of state based on the well-known PHS scheme was utilized to model the volumetric properties of some ethylene glycol-, poly ethylene glycol-, water-, poly ethylene glycol+water- and ethylene glycol+water-based nanofluids at compressed states and different nanoparticle concentrations. “Generally, we proceeded in three steps:

- 1) Starting with pure-components including base fluids and nanoparticles
- 2) Estimation of pure-component parameters
- 3) Extension of PHS model to mixed base fluids and nanofluids by the help of crossed interaction parameters.

Although the evaluation of $a(T)$ and $b(T)$ parameters demands the relevant pair-potential function operating between the nanoparticles and the base fluid molecules, this work showed that these parameters can be evaluated through a corresponding

states correlation scheme together with some simple combining rules for the mixed fluid.

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Nomenclature and units

b (T)	van der Waals co-volume, m^3
P	pressure, Pa
R	gas constant, J/mole. K
T	absolute temperature, K
k_B	Boltzmann's constant, J/K
M_w	molecular weight
a (T)	strengths of attractive forces, J/m^3
a_1 - a_4	the coefficients that used in Eq. (8)
b_1 - b_4	the coefficients that used in Eq. (9)
F_a and F_b	universal functions
N_A	Avogadro's number
V^E	excess volume/ $\text{cm}^3 \text{ g}^{-1}$
x	mole fraction
k_{12}	binary interaction parameters operating unlike base fluid molecules
$k_{\text{np-bf}}$	binary interaction parameter raised by nanoparticle surface and base fluid molecule interaction
Greek letters	
ε	non-bonded interaction energy parameter/ J
σ	effective hard-sphere diameter/ nm
η	packing fraction
ρ	molar density, mol/m^3
κ_T	isothermal compressibility/ Pa^{-1}
φ	nanoparticle mass fraction
Subscripts	
np	nanoparticle
bf	base fluid
EOS	derived from an equation of state
Superscripts	
Calc	calculated
Exp	experimental

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Table 1 The molecular scaling constants of based fluids and nanoparticles of interest to be used in Eqs. (6)-(9).

Pure base fluid	$M_W(\text{g/mol})^a$	$\varepsilon/k_B(\text{K})$	$\sigma(\text{nm})$	$\Delta T/\text{K}$	$\Delta P/\text{MPa}$	NP ^b	AAD (%) ^c	Ref.
EG	62.07	1673.5	0.43231	283-323	0.1-45	54	0.53	[53]
water	18.03	881.55	0.2826	280-380	0.1-50	110	1.07	[51]
PEG	60.00	659.7	0.3980	298-328	0.1-45	40	0.76	[52]
Nanoparticle	$M_W(\text{g/mol})$	$\varepsilon/k_B(\text{K})$	$\sigma(\text{nm})$	ATD ^e /g cm ⁻³		TD ^d /g·cm ⁻³	T_m/K^f	
ZnO	81.40	3109.2	0.28608	5.58		5.60	1975	
SnO ₂	150.69	2588.3	0.32446	6.87		6.95	1630	
TiO ₂ -Rutile	79.93	3002.3	0.3105	4.22		4.23	1870	
TiO ₂ -Anatase	79.93	2935.3	0.3105	4.18		3.90	1843	
Co ₃ O ₄	74.93	1650.3	0.26046	6.01		6.11	895	
Al ₂ O ₃	101.96	3459.2	0.3484	3.87		3.90	2040	
CuO	79.545	1856.3	0.26354	6.39		6.31	1201	

^a molecularweight

^b NP represents the number of data points examined

$$^c \text{AAD} = 100/\text{NP} \sum_{i=1}^{\text{NP}} | \rho_i^{\text{Exp.}} - \rho_i^{\text{Calc.}} | / \rho_i^{\text{Exp.}}$$

^d TD represents the true densities of nanoparticle which have been taken from literature [54]

^e ATD represents the average true densities of nanoparticle reproduced from PHS EOS

^f these values were taken from literature [54].

Table 2 The AAD (in %) of predicted densities of studied mixed base fluids and nanofluids using the proposed PHS EOS from the measurements.

Mixed base fluid	ΔP (MPa)	ΔT (K)	Δx_{water}	NP ^a	k_{12}	AAD ^b (%)	Ref.
EG+water	0.1-0.1	278-363	0.0 -1.0	44	0.038	0.20	[58]
	0.1-45	278-323	0.755-0.755	54	0.038	0.65	[56]
PEG+water	0.1	293-318	0.0 -1.0	77	0.38	1.94	[57]
Nanofluid	ΔP (MPa)	ΔT (K)	Δx_{np}	NP ^a	$k_{\text{np-bf}}$	AAD ^b (%)	Ref.
TiO ₂ -R/EG	0.1-45	283-343	0.014-0.039	30	0.210	0.06	[59]
TiO ₂ -A/EG	0.1-45	283-343	0.014-0.039	30	0.343	0.05	[59]
SnO ₂ /EG	0.1-45	283-323	0.004-0.021	270	0.030	0.05	[53]
Co ₃ O ₄ /EG	0.1-45	283-323	0.009-0.048	270	0.390	0.08	[61]
CuO/water	0.1-45	283-323	0.002-0.012	450	0.051	0.54	[62]
ZnO/EG+water	0.1-45	278-363	0.009-0.038	110	-0.625 ^c	1.23	[56]
	0.1	273-323	0.021-0.041	42	0.619 ^d	0.58	[25]
Al ₂ O ₃ /EG+water	0.1	273-323	0.012-0.107	42	-0.003	1.10	[25]
ZnO/PEG	0.1	293-318	2E ⁻⁴ -0.077	56	0.610	1.69	[60]
ZnO/PEG+water	0.1	293-318	9E ⁻⁵ -0.016	48	0.610	0.50	[60]
Overall					1348	0.44	

^a NP represents the number of data points examined

$$\text{AAD} = 100/\text{NP} \sum_{i=1}^{\text{NP}} |\rho_i^{\text{Exp.}} - \rho_i^{\text{Calc.}}| / \rho_i^{\text{Exp.}}$$

^cthese values were obtained for suspensions cantoning ZnO nanoparticle with the average particle size (APS) equal to 29 nm.

^dthese values were obtained for suspensions cantoning ZnO nanoparticle with APS equal to 70nm.

Figure Captions

Figure 1 The linear correlations of melting temperatures[54]with ε/k_B (**a**-plot) as well as true densities versus $M_w (N_A\sigma^3)$ (**b**-plot) for studied nanoparticles. The open markers represent our estimations and solid line indicates the best straight line passing through the points.

Figure 2 The linearity of the nanofluid densities versus pressure for SnO₂/EG (at $x_{np}=0.0147$) and TiO₂-R/EG (at $x_{np}=0.0136$ and 0.039) at several isotherms; for **a**-plot at 283K ($\diamond$), 303K (Δ) and 323K ($\circ$); For **b**-plot at 283k ($\diamond$), 323K(Δ) and 343K ($\circ$). The markers represent the experimental isotherms of Mariano et al. [53] and Cabaleiro et al. [59], solid lines are those predicted using the proposed PHS EOS.

Figure 3 Plots of isothermal compressibilities vs. pressure for some selected nanofluids including TiO₂-R/EG at $x_{np}= 0.0136$ (**a**-plot), TiO₂-R/EG at $x_{np}= 0.039$ (**b**-plot) and ZnO/EG+ water at $x_{np}=0.0183$ (**c**-plot). The solid lines are our predictions and markers are isotherms of Cabaleiro et al. [56, 59]. **a**-plot represents the results at 303 K (Δ), 323 K ($\square$) and 343 K ($\diamond$). **b- and c**-plots represent the results at 283 K (Δ), 313 K ($\square$) and 343 K ($\diamond$).

Figure 4 Plots of thermal expansion coefficient vs. pressure for ZnO/EG+ water at $x_{np}=0.0183$ (**a**-plot) and $x_{np}=0.0378$ (**b**-plot). The solid lines are our predictions and markers are isotherms of Cabaleiro et al. [56] at 303 K ($\diamond$), 323 K ($\square$), and 343 K (Δ).

Figure 5 Plots of isothermal excess volumes against nanoparticle mass fractions (ϕ in %), for three selected nanofluids including SnO₂/EG (**a**-plot), Co₃O₄/EG (**b**-plot) and CuO/water (**c**-plot) at atmospheric pressure as well as 10 MPa. The solid lines are our predictions and markers are isotherms of Pastoriza-Gallego et al.[62] and Mariano et al. [53, 61].For **a**-plot, the data were taken from 0.1 MPa at 283 ($\diamond$),10 MPa at 323K ($\square$).For **b**-plot, the data were taken from 0.1 MPa at 283 ($\diamond$), 10 MPa at 323K (*). For **c**-plot, the data were taken from 0.1 MPa at 283 ($\diamond$), 10 MPa at 323K ($\square$).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5