A critical investigation of the anomalous behavior of molten salt-based nanofluids ☆

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ABSTRACT

A critical investigation is presented in this work to study the effect of nanoparticle addition, temperature, and nanoparticle size-dependence on the specific heat capacity of both conventional and molten salt-based nanofluids. The effects of temperature and nanoparticle volume fraction on the specific heat capacity of conventional nanofluids are in agreement in all studies cited in this review. Different correlations based on the available data were developed as a function of temperature and volume concentration only. However, the effect of nanoparticle size-dependence was ignored in these correlations. A general correlation for Al_2O_3–water nanofluids, one of the most commonly studied nanofluids, that takes into account the effect of temperature, volume fraction, and nanoparticle size-dependence was developed and verified in this review. Disagreement was reported for the results of the specific heat capacity of molten salt-based nanofluids. A number of studies showed an enhancement in the specific heat capacity of nanofluids using 1% concentration of nanoparticles by weight only. However, other studies have shown deterioration in the specific heat capacity of nanofluids compared with the base mixture using various volume concentrations of nanoparticles. Moreover, very few studies have demonstrated the effect of nanoparticle size-dependence on the specific heat capacity of molten salt nanofluids and disagreement in the results was reported in these studies. Few models based on the conventional specific heat model were developed to determine the specific heat capacity of molten salt nanofluids. These models suffer from the lack of knowledge of many terms in these equations which make them impractical. Different mechanisms were assumed in the literature to explain the abnormal behavior of molten salt nanofluids. Additional theoretical and experimental research studies are required to clarify the mechanisms responsible for specific heat capacity enhancement or deterioration in nanofluids.

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1. Introduction

Recent advances in nanotechnology have led to the development of an innovative class of heat transfer fluids (nanofluids) created by dispersing nanoparticles (10–50 nm) in traditional heat transfer fluids. Nanofluids show the potential to significantly increase heat transfer rates in a variety of areas. A significant number of studies associated with heat transfer enhancement using nanofluids has been conducted by many researchers [1–14]. The thermal properties of nanofluids such as thermal conductivity, specific heat capacity, viscosity, nucleate pool boiling heat transfer coefficient, and critical heat flux have been studied. Khanafer and Vafai [3] presented a critical synthesis of the variants within the thermophysical properties of nanofluids. They demonstrated that the experimental results for the effective thermal conductivity and viscosity reported by several

authors are in disagreement. Correlations for the effective thermal conductivity and viscosity were synthesized and developed in their study in terms of pertinent physical parameters based on the reported experimental data.

While many studies in literature have reported enhanced effective thermal conductivity of nanofluids, specific heat capacity measurements have shown controversial results [3,15–27]. Zhou and Ni [18] presented an experimental study of the specific heat of water-based Al_2O_3 nanofluid. Their results indicated that the specific heat of nanofluids decreased gradually as the nanoparticle volume fraction increased. Das and co-workers [15–17] found reduced specific heats of nanofluids consisting of silicon dioxide, zinc oxide, and alumina nanoparticles, respectively, dispersed in a mixture of water and ethylene glycol as compared to that of the base fluid. Moreover, they experimentally illustrated that the specific heat value of the nanofluid increases moderately with an increase in temperature [17]. Zhou et al. [19] indicated that the specific heat capacity of CuO nanofluid decreased gradually with increasing volume concentration of nanoparticles. Khanafer and Vafai [3] have demonstrated analytically and verified experimentally

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[19] that the addition of nanoparticles decreases the specific heat capacity of nanofluid at room temperature. Sundar et al. [20] estimated experimentally specific heat capacity values of Al_2O_3 nanofluid at different concentrations and at different temperatures. They have shown that the specific heat of the Al_2O_3 nanofluid decreases with an increase in the nanoparticle volume fraction.

Furthermore, several studies in the literature have demonstrated disagreement in the specific heat capacity results of molten salt doped with nanoparticles [21–27]. Nelson et al. [21] reported that the specific heat of nanofluids (exfoliated graphite nanoparticle fibers suspended in polyalphaolefin at mass concentrations of 0.6 and 0.3%) was found to be 50% higher compared with pure polyalphaolefin. Shin and Banerjee [22] conducted an experimental study showing the effect of dispersing silica nanoparticles (1% by weight) for enhancing the specific heat capacity of the eutectic of lithium carbonate and potassium carbonate (62:38 ratio). A differential scanning calorimeter instrument was used to measure the specific heat of the molten salt eutectic after addition of nanoparticles. They found that the specific heat of the nanofluid was enhanced by 19–24%. Chieruzzi et al. [26] experimentally studied the effect of nanoparticles on heat capacity of nanofluids based on molten salts as PCM for thermal energy storage. The base salt mixture was a $NaNO_3$–KNO_3 (60:40 ratio) binary salt and the nanoparticles used were silica (SiO_2), alumina (Al_2O_3), titania (TiO_2), and a mix of silica–alumina (SiO_2–Al_2O_3). Thermophysical property measurements were performed by differential scanning calorimetry analysis and the dispersion of the nanoparticles was analyzed by scanning electron microscopy (SEM). Their obtained results showed that the addition of 1.0 wt.% of nanoparticles to the base salt increased the specific heat by 15% to 57% in the solid phase and by 1% to 22% in the liquid phase. The authors referred this enhancement to the high specific surface energies associated with the high surface area of the nanoparticles per unit volume. Surprisingly, concentrations lower and higher than 1.0 wt.% of nanoparticles showed specific heat capacity deterioration compared with base salt mixture of NaNO3-KNO3 (60:40). Lu and Huang [27] showed that the specific heat of the molten salt-based alumina nanofluids decreased with increasing particle concentration.

Various correlations were developed in the literature to estimate the specific heat capacity of water-based nanofluids as a function of

temperature and volume fraction of nanoparticles. The size-dependence of Al_2O_3 nanoparticles was ignored. The aim of this investigation is to develop a robust correlation based on the available experimental data for the specific heat of water-based nanofluids as a function of various pertinent parameters and propose possible physical reasons for the deviations between the experimental data and the analytical model-based thermal equilibrium of the specific heat capacity.

One can notice from the cited literature that there are controversial results reported for the specific heat of molten salt nanofluids. Further theoretical and experimental research is needed in order to explain this disagreement in the results. Various possible mechanisms were proposed in the literature without any theoretical or experimental validation. However, there is no robust description of the anomalous behavior of molten salt-based nanofluids including enhancement or deterioration of the specific heat capacity. The specific heat capacity of molten salt-based nanofluids data is still contradictory in various research publications. Another objective of this study is to discuss the variants within different mechanisms that describe the anomalous behavior of the specific heat capacity of nanofluids and propose possible physical reasons for the deviations between experimental and analytical studies.

2. Specific heat capacity of conventional nanofluids

The vast majority of studies on conventional nanofluids have used an analytical model for the specific heat by assuming thermal equilibrium between nanoparticles and the base fluid phase as follows:

$$(\rho c)_{eff} = \rho_{eff} \left(\frac{Q}{m \Delta T} \right)_{eff} = \rho_{eff} \frac{Q_f + Q_p}{(m_f + m_p) \Delta T} = \rho_{eff} \frac{(mc)_f \Delta T + (mc)_p \Delta T}{(m_f + m_p) \Delta T}$$
$$\rightarrow (\rho c)_{eff} = \rho_{eff} \frac{(\rho c)_f V_f + (\rho c)_p V_p}{\rho_f V_f + \rho_p V_p}$$
$$\Rightarrow c_{eff} = \frac{(1 - \phi_p) \rho_f c_f + \phi_p \rho_p c_p}{\rho_{eff}}$$

$$(1)$$

where ρ_p is the density of the nanoparticle, ρ_f the density of the base fluid, c_p and c_f are the heat capacities of the nanoparticle and the base
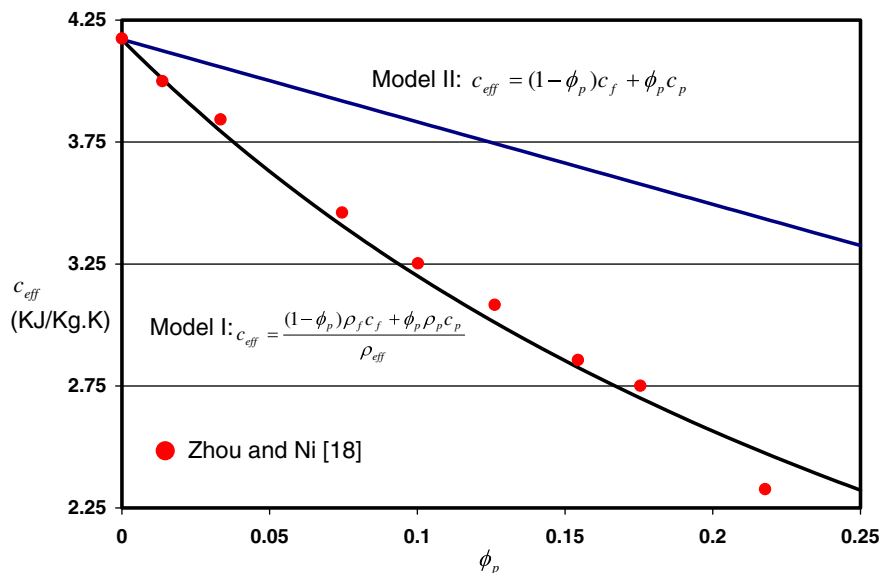

Fig. 1. Comparison of the heat capacity of Al_2O_3–water nanofluid obtained by models I and II given in Eqs. (1) and (2) and the experimental data of Zhou and Ni [18] (Reprinted from Khanafer and Vafai [3] with permission from Elsevier).

fluid, respectively, and $\rho_{eff} = (1 - \phi_p)\rho_f + \phi_p\rho_p$ is the density of the nanofluids. On the other hand, some authors [28–31] suggest a simpler expression given by:

$$c_{eff} = \left(1 - \phi_p\right)c_f + \phi_p c_p. \tag{2}$$

The experimental data of Zhou and Ni [18] was used to evaluate the validity of Eqs. (1) and (2). Fig. 1 shows a comparison of the specific heat of Al$_2$O$_3$–water nanofluid at room temperature using both equations with the experimental data of Zhou and Ni [18] for various volume fractions ($\phi_p = 0$–21.7%). Fig. 1 shows that model given in Eq. (1) compares very well with the experimental data of Zhou and Ni [18]. An additional check on the accuracy of Eq. (1) when determining the effective specific heat of conventional nanofluids is shown in Fig. 2. The results of Barbés et al. [32] agreed well with the conventional effective specific heat model based on thermal equilibrium.

2.1. Effect of temperature on the specific heat capacity of conventional nanofluids

Studies were also conducted in the literature to investigate the effect of temperature variation on the specific heat capacity of nanofluids [17, 32–34]. The results presented in these investigations demonstrated that the specific heat capacity of nanofluids increases with an increase in the temperature. Different correlations were obtained from the experimental data. For example, Vajjha and Das [17] presented a correlation developed from the experimental measurements of the specific heat of Al$_2$O$_3$, ZnO, and SiO$_2$ nanofluids as follows:

$$\frac{c_{eff}}{c_f} = \frac{A \times T + B \times \dfrac{c_p}{c_f}}{C + \phi_p}. \tag{3}$$

The curve-fit coefficients (A, B, and C) for each nanofluid are tabulated in Table 1. This equation is applicable over the temperature range of 315 < T(K) < 363 for volumetric concentrations ranging: 0 < ϕ_p ≤ 0.1 for Al$_2$O$_3$ and SiO$_2$ nanofluids and 0 < ϕ_p ≤ 0.07 for ZnO nanofluid. The samples of Al$_2$O$_3$, ZnO, and SiO$_2$ nanofluids used by Vajjha and Das [17] had average particle sizes of 44 nm, 77 nm, and 20 nm, respectively.

Table 1
Coefficients in Vajjha and Das Model [17].

Nanoparticles	Coefficients		
	A	B	C
Al$_2$O$_3$	0.0008911	0.5179	0.4250
SiO$_2$	0.001769	1.1937	0.8021
ZnO	0.0004604	0.9855	0.299

Yiamsawasd et al. [34] conducted an experimental study to determine the specific heat capacity of nanofluids using TiO$_2$ and Al$_2$O$_3$ nanoparticles in pure water and a mixture of ethylene glycol/water (20/80 wt.%). Volume fractions between 0 and 8% and temperatures between 15 °C and 65 °C were used. The experimental results indicated that the specific heat of nanofluids was lower than the base fluid and tends to decrease when concentration increases. On the other hand, an increase in the temperature caused the specific heat of the nanofluids to increase. The authors developed a correlation based on their experimental data to determine the specific heat of TiO$_2$ and Al$_2$O$_3$ nanofluids as a function of temperature, volume fraction, specific heat of nanoparticles, and the specific heat of the base fluid as follows:

$$\frac{c_{eff}}{c_f} = A\phi_p^B T^C \left(\frac{c_p}{c_f}\right)^D, \ 15 \le T(^\circ C) \le 65 \ \text{and} \ 1 \le \phi \le 8\% \tag{4}$$

where A, B, C, and D are the coefficients shown in Table 2. The average diameter of the TiO$_2$ particles was 21 nm and the average diameter of the Al$_2$O$_3$ particles was 120 nm.

Barbés et al. [32] determined experimentally the specific heat capacities of Al$_2$O$_3$ nanoparticles dispersed in water and ethylene glycol and water as a function of the particle volume fraction (0.037 ≤ ϕ_p ≤ 0.093) and at temperatures between 298 and 338 K. A correlation was developed for the specific heat capacity of Al$_2$O$_3$–water nanofluids based on the experimental results of Barbés et al. [32] by the present authors as follows:

$$c_{eff} = 4.1002 + 0.051\phi_p \times (-244.3107 + 0.2249T); \ \text{kJ/kg K}. \tag{5}$$

The average particle size of Al$_2$O$_3$–water nanofluids used in that study was 45 nm.

Utilizing various experimental data, we have developed a general correlation (Eq. (6)) for the effective specific heat capacity of Al$_2$O$_3$–
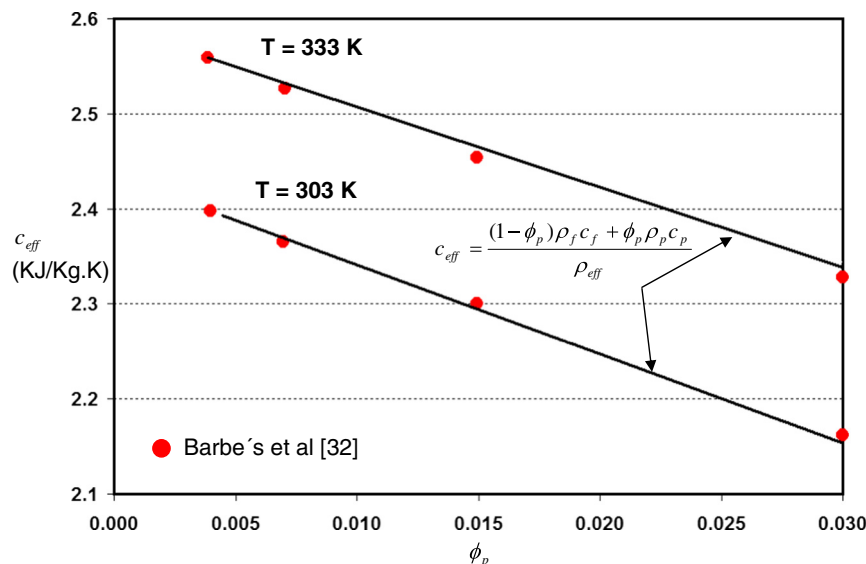

Fig. 2. Comparison of the specific heat capacity of CuO/ethylene glycol nanofluid obtained by Eqs. (2) and the experimental data of Barbés et al. [32].

Table 2
Coefficients in Yiamsawasd et al. [33] Model.

Nanoparticles	Coefficients			
	A	B	C	D
Al_2O_3	1.249458	−0.05846	0.006467	−0.17236
TiO_2	1.387402	−0.06425	0.001124	−0.21159

water nanofluid, one of the most commonly studied as a function of volume fraction, nanoparticle diameter, and temperature as follows:

$$c_{eff} = 7.4309 - \frac{1073.6563}{T} - 39.4291\phi_p + 202.6344\phi_p^2 - 6.19 \times 10^7 \frac{\phi_p^2}{T^2} + 3369.3060\phi_p^3$$
$$+ 1.34 \times 10^9 \frac{\phi_p}{T^3} + 1.18 \times 10^5 \frac{\phi_p^2}{d_p^2} - 1.34 \times 10^6 \frac{\phi_p^3}{d_p^2}$$
$$0.01 \le \phi_p \le 0.1, \ 288 \le T(K) \le 360, \ 44\,nm \le d_p \le 120\,nm.$$

(6)

The R^2 of the regression is 98%. The validity of the above correlation (Eq. (6)) is depicted in Fig. 3. It can be seen that as the diameter of nanoparticles increases, the specific heat capacity of Al_2O_3–water nanofluids

decreases. Eq. (6) is the first developed correlation in the literature that shows explicitly the effect of various pertinent parameters on the specific heat capacity. The other developed correlations reported in the literature [17,32,34] did not include the effect of nanoparticle diameter in their equations.

As mentioned earlier model for calculating the specific heat of nanofluids, assumes thermal equilibrium between nanoparticles and the base fluid [3] as reported by Eq. (1). However, Eq. (1) does not include the effect of nanoparticle diameter on the effective specific heat capacity of nanofluids. Fig. 4 shows a comparison of the effective specific heat capacity of Al_2O_3–water nanofluid between the results obtained using Eqs. (6) and (1). It is clearly noticed in Fig. 4 that Eq. (1) underestimates the specific heat of nanofluid.

2.2. Specific heat capacity of molten salt-based nanofluids

The demand for energy and electricity increases as the global economy continues to grow. However, higher fuel prices, lack of grid infrastructure investment, safety issues with nuclear power plants, and the desire to minimize CO_2 emissions are some of the reasons for replacing
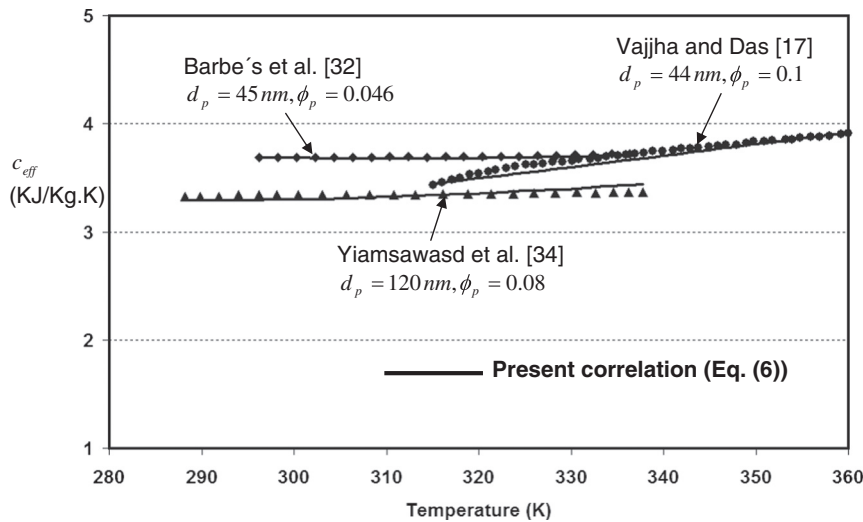

Fig. 3. Comparison of Eq. (6) developed in the current work with the experimental data. Effect of the volume fraction, nanoparticle diameter, and temperature on the effective specific heat capacity of Al_2O_3–water nanofluid.
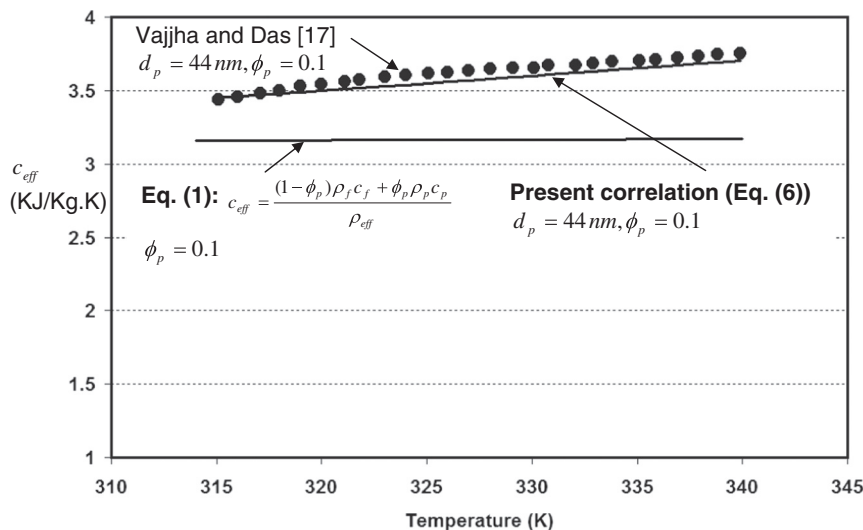

Fig. 4. Comparison of the effective specific heat capacity of Al_2O_3–water nanofluid between the results obtained using Eqs. (6) and (1).

fossil fuels with renewable energy. Renewable energy production is irregular and the power output depends on weather and location. Fossil fuel generation can be turned on or off on a need basis, while shifting to renewable energy generation needs management of demand and supply. As such, thermal energy storage (TES) systems are essential to store the generated renewable energy. TES enables the electric grid to overcome the intermittent power output of renewable energy, keeping the electric grid stable and reliable.

The efficiency and reliability of solar thermal energy conversion systems depend significantly on the specific heat of the heat transfer fluid (HTF) as well as on the operating temperature of the thermal energy storage systems. The operating temperature of a conventional TES system is restricted not to exceed 400 °C due to the limitation of the materials used in TES systems such as mineral oil and fatty acids [35]. Molten salt has been recently used in concentrated solar power (CSP) facilities because it is stable at very high temperatures, i.e., exceeding 600 °C [22,36] and can store more heat than the synthetic oil used in the CSP and therefore produces electricity even after the sun has gone down. Typical molten salt materials include alkali-carbonate, alkali-nitrate, alkali-chloride, or their eutectic [36]. The use of molten salt as a heat transfer fluid in solar plants increases the Rankine cycle efficiency of the power steam turbine (from 54% at 400 °C to 63% at 560 °C [36]) and may reduce the physical size of the thermal storage system for a given capacity. In addition, molten salt is cheap and more environmentally safe than the present HTFs [22]. The major challenge of molten salt is its high freezing point, leading to complications related to freeze protection in the solar field. In addition, molten salts exhibit poor thermophysical properties (e.g. specific heat capacity ~1.55 J/gK at 350 °C and thermal conductivity ~1 W/mK, while the specific heat of water is 4.2 J/gK at room temperature) which may increase the size requirement of TES.

The application of high temperature nanofluids in the form of molten salts doped with nanoparticles in thermal storage systems is essential for continuous operation of solar thermal power plants. The enhanced specific heat capacity of the nanofluids can significantly reduce the required amount of thermal energy storage media in solar power plants and may reduce the electricity cost. Although several studies in the literature showed that the specific heat capacity of conventional nanofluids decreased with an increase in particle volumetric concentration, a number of molten-based nanofluids showed contradictory results regarding the enhancement of specific heat capacity [21–27]. Shin and Banerjee [23] reported the anomalous enhancement of specific heat capacity of high-temperature nanofluids. Alkali metal chloride salt eutectics were doped with silica nanoparticles at a fixed mass concentration of 1%. The specific heat capacity of the nanofluid was enhanced by 14.5%. The same authors [24] proposed three thermal mechanisms to explain the abnormal enhancement of the specific heat capacity. These mechanisms include: (1) higher specific heat capacity of nanoparticles compared with the bulk value of the base fluid, (2) fluid–solid interaction energy, and (3) "layering" of liquid molecules at the surface to form a semi-solid layer.

The mechanisms proposed by Shin and Banerjee [24] were similar to the mechanisms proposed by Keblinski et al. [37] to explain the thermal conductivity enhancement of nanofluids. Tiznobaik and Shin [25] dispersed four different sized silicon-dioxide nanoparticles (5, 10, 30, and 60 nm in diameter) in a molten salt eutectic of lithium carbonate and potassium carbonate (Li_2CO_3–K_2CO_3, 62:38 by molar ratio) to obtain high temperature operating fluids. These authors showed a 25% enhancement in the specific heat of nanofluids (1% mass concentration) regardless of the size of the embedded nanoparticles. The authors attributed this enhancement to the formation of needle-like structures (very large specific surface area) induced by the addition of nanoparticles, which can be seen in Fig. 5. However, Lu and Huang [27] showed that the specific heat capacity of molten salt-based alumina nanofluids decreased with an increase in the volume fraction of nanoparticles, which is similar to previous studies on conventional nanofluids.

3. The anomalous behavior of molten salt-based nanofluids

Different mechanisms were proposed in the literature to explain the anomalous behavior of the specific heat capacity of molten salt-based nanofluids. Such mechanisms include enhanced specific heat capacity of nanoparticles [27,38,39], formation of a nanolayer [22–25,40–42], solid–fluid interaction energy [40,43], and the formation of fractal-like fluid nanostructures [25,44,45].

3.1. Enhanced specific heat capacity of nanoparticles

Wang et al. [38] conducted an experiment to study the enhancement of the specific heat capacity of nanosized alumina (average particle size of 20 nm). Their results showed that heat capacities of nanosized Al_2O_3 had large excess heat capacity from 6% to 23% as compared to the coarse-grained one in the temperature range of 200–370 K. Moreover, Wang et al. [39] reported that the specific heat capacity of nanoparticles increased when the size of nanoparticles (CuO) decreased using a theoretical model.

Lu and Huang [27] analyzed the effect of nanoparticles addition on the specific heat capacities of molten salt (60-wt.% NaNO3 and 40-wt.% KNO3) doped with alumina nanoparticles and molten salt-based alumina nanofluids. Their experimental results show that the specific heat capacity of alumina nanoparticles increased by ~20.5% at a temperature of 350 K when the particle size decreases from 90 nm to 13 nm. Moreover, they found that the specific heat of alumina nanoparticles increases with temperature while the temperature effect on the specific heat capacities of the molten salt and the nanofluids (molten salt-based alumina) is insignificant. This was also shown in other studies
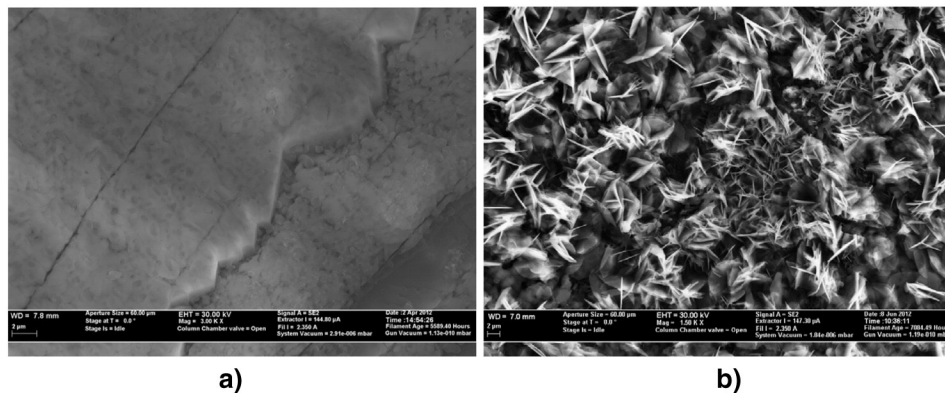

Fig. 5. (a) Scanning electron micrograph (SEM) of pure eutectic mixture after testing and (b) scanning electron micrograph (SEM) of nanomaterial (30 nm) after testing. Special needle-like structures are formed all over the nanomaterials (Reprinted from Tiznobaik and Shin [25] with permission from Elsevier).

[22–25]. The authors [27] also demonstrated that the specific heat capacity of molten salt-based alumina nanofluids decreases with an increase in the volume fraction of nanoparticles, which is similar to previous studies on conventional nanofluids [15–19]. Furthermore, the effective specific heat capacity of nanofluids was found experimentally to decrease with a reduction in the particle size.

However, Tiznobaik and Shin [25] reported an increase in the specific heat capacity results of nanofluids. Their experimental results showed that the specific heat capacity of nanofluids (molten salt-based silicon dioxide) was enhanced by 25% over that of the base molten salt eutectic (base fluid), regardless of the size of embedded silicon-dioxide nanoparticles (5, 10, 30, and 60 nm in diameter). Jung and Banerjee [46] showed analytically that the specific heat capacity of nanofluids containing carbon nanotube (CNT) nanoparticles dispersed in a liquid phase of alkaline metal carbonate salt eutectic mixture (Li$_2$CO$_3$–K$_2$CO$_3$ in 62:38 molar ratio) decreased with an increase in the diameter of nanoparticles. Insignificant enhancement of the specific heat of the nanofluids was found for nanoparticle diameter exceeding 20 nm.

The specific heat enhancement of nanoparticles may be explained by the Debye model of heat capacity of solids [47]. In thermodynamics and solid state physics, the Debye model was a method developed by Peter Debye in 1912 for estimating the phonon contribution to the specific heat in a solid. It was found that the Debye temperature decreases, which is the highest temperature that can be achieved due to a single normal vibration, with reducing particle size, resulting in an increased specific heat capacity. The size-dependent specific heat capacity of nanoparticles was also observed in other studies [48,49]. It is well documented that the specific surface area is considered an important parameter in many applications. As the specific surface area increases with a decrease in the particle size, the specific surface energies can be increased and subsequently the nanoparticles may have higher thermal characteristics [38,39] compared with that of the bulk fluid and this may contribute to the enhanced specific heat capacity of nanofluids.

3.2. Nanolayer at solid/liquid interface

The formation of solid-like nanolayer of liquid molecules around nanoparticles is assumed in many studies to contribute to the enhancement of thermal conductivity of nanofluids [40,42,50]. Various models based on classical effective medium theories [42,52] were developed in the literature to estimate its effect. However, there is a certain lack of information regarding the thickness of these layers and the associate increase in the thermal conductivity. For example, Lin et al. [40] studied the effect of the molecular layering at the liquid–solid interface on the thermal conductivity of nanofluids by an equilibrium molecular dynamics simulation. They found that the nanolayer structure was size-dependent. As such, a nanofluid with larger nanoparticles will result in a larger enhanced thermal conductivity.

The solid-like nanolayer around the surface of the nanoparticles is also hypothesized to be one of the mechanisms that may contribute to the enhancement of specific heat capacity of molten salt-based nanofluids. This layer often has higher thermo-physical properties than the bulk fluid. In particle–fluid mixtures, the liquid molecules close to a particle surface are known to form layered structures and behave like a solid [40,41,51]. The thickness of this aligned solid-like layer of liquid molecules at the interface is at a magnitude of nanometer, but this nanolayer might play a significant role in heat transport from solid to nearby liquid [52]. For example, the specific surface area of alumina powders with an average diameter of 10 μm is 0.15 m^2/g while it is 151 m^2/g for alumina nanoparticles with an average diameter of 10 nm [52]. The nanolayer at the solid/liquid interface can result in an enhanced heat transfer across the interface and ultimately may result in an increased specific heat capacity of the nanofluids.

There are only few studies related to modeling the effect of a nanolayer on the specific heat capacity of molten salt-based nanofluids [27,46]. Jung and Banerjee [46] proposed a simple analytical model to determine the specific heat capacity of molten slat-based nanofluids. The nanolayer formed in the solvent was assumed to envelope the nanoparticles. The specific heat capacity was given by:

$$c_{eff} = \frac{(Mxc_p) + \left(\frac{Mx}{m_p}m_{nanolayer}c_{nanolayer}\right) + \left[\left(M - Mx - \frac{Mx}{m_p}m_{nanolayer}\right)c_f\right]}{M}$$
(7)

where M is the total mass of nanofluids, x is the mass concentration of the nanoparticles in the mixture, m_p is the mass of a nanoparticle, and $m_{nanolayer}$ is the mass of the nanolayer. The mass of a nanoparticle was expressed as:

$$m_p = \rho_p V_p = \rho_p \pi \left(\frac{D_p}{2}\right)^2 L_p$$
(8)

where ρ_p and V_p are the density and volume of an individual nanoparticles of diameter D_p and length L_p, respectively.

The mass of nanolayer surrounding an individual nanoparticle can be expressed as [46]:

$$m_{nanolayer} = (\rho V)_{nanolayer}$$
$$= \rho_{nanolayer}\pi \left[\begin{array}{l}\left(\frac{D_p}{2} + t_{nanolayer} + t_{void}\right)^2 (L_p + t_{nanolayer} + t_{void}) \\ -\left(\frac{D_p}{2} + t_{void}\right)^2 (L_p + t_{void})\end{array}\right]$$
(9)

where $t_{nanolayer}$ and t_{void} are the thickness of nanolayer and the void space, respectively. A void space was assumed to exist between the nanoparticles and the nanolayer, due to the van der Waals equilibrium distance. To determine the specific heat capacity of molten salt-based alumina, Lu and Huang [27] modified Eq. (1), which is based on the thermal equilibrium between nanoparticles and the base fluid, to take into an account the effect of nanolayer as follows:

$$c_{eff} = \frac{c_p W_p + c_{nanolayer}W_{nanolayer} + c_f(W_f - W_{nanolayer})}{W_f + W_p}$$
(10)

where W is the weight. Based on Eq. (10) as nanoparticle concentration increases, the weight of nanolayers increases and consequently reduces specific heat capacity of nanofluids, provided that the nanolayer has a lower specific heat than molten salt.

3.3. Formation of fractal-like fluid nanostructures

In addition to the above mechanisms, a number of studies on studying the specific heat capacity of molten slat-based nanofluids observed fractal-like fluid nanostructures (needle-like structures) [22–25,45,53]. These nanostructures are characterized by very large specific surface areas similar to nanoparticles. It was reported by many researchers that specific heat capacity presumed to be enhanced when specific surface area is substantially increased when nanoparticles are utilized [38, 39]. Shin and co-authors [25,45,53] postulated that the effective specific heat capacity of molten salt nanofluids may be significantly enhanced when fractal-like fluid nanostructures are formed by nanoparticles. Hence, Eq. (1) was modified to include the effect of fractal-like fluid nanostructure as follows [45,53]:

$$c_{eff} = \frac{m_{fractal}c_{fractal} + m_p c_p + m_{\bar{f}}c_{\bar{f}}}{m_{\bar{f}} + m_p + m_{fractal}}$$
(11)

where m is the mass fraction and $\bar{f}$ is the remaining base fluid (exclusion of fractal-like fluid nanostructure). These authors conducted their experiments using a mass concentration of 1%. The main drawback of

this equation is that the specific heat capacity and mass fraction of nano-structures are unknowns and therefore, the properties of fractal-like fluid nanostructure need to be experimentally determined.

The results reported in the literature on the specific heat capacity of molten salt-based nanofluids are in disagreement as cited earlier, for example, Lu and Huang [27] found that the specific heat capacity of molten salt-based nanofluids decreases when the nanoparticle size decreases and the volume concentration increases. However, Tiznobaik and Shin [25] showed a 25% enhancement in the specific heat capacity of nanofluids at 1% concentration by weight regardless of the nanoparticle sizes. Chieruzzi et al. [26] showed an enhancement in the specific heat capacity of nanofluids with an addition of 1% concentration by weight of nanoparticles to the base salt, which confirmed the results of Tiznobaik and Shin [25]. However, concentrations lower and higher than 1% by weight displayed a decrease in the specific heat capacity of nanofluids compared to the base salt mixture. This contradiction in the reported results requires further experimental studies to show thoroughly the effect of volume concentration, nanoparticle diameter size and temperature on the specific heat capacity of molten salt-based nanofluids.

Few models were proposed in the literature to determine the specific heat capacity of molten salt-based nanofluids. These models were based either on a simplified theoretical model [46] or based on the conventional specific heat model (Eq. (1)). The equation model proposed by Shin and co-authors [25,45,53] is impractical since it requires information on the specific heat capacity of the needle-like structures and mass fraction which cannot be determined either experimentally nor theoretically. Also, the geometrical characteristics of the needle-like structures will vary from one mass concentration to another. The model proposed by Lu and Huang [27] also utilized Eq. (1) to include the effect of nanolayer on the specific heat capacity of nanofluids. In that model (Eq. (10)), it was assumed that the specific heat capacity of nanofluids is the superposition of the specific heat capacities of nanolayer, nanoparticles, and the base fluid. This model requires the knowledge of the specific heat capacity and thickness of nanolayer for various nanoparticle sizes.

Therefore, to the best of our knowledge, no robust model is available in the literature that explains the anomalous behavior of molten salt-based nanofluids. More experimental and theoretical studies are required for various pertinent parameters such as nanoparticle size, volume fraction concentration, temperature, and various base fluid and nanoparticles.

4. Conclusions

Different studies were conducted in the literature to study the effect of nanoparticle addition on the specific heat capacity of nanofluids. Unanimous agreement was found among various studies on the effect of temperature and nanoparticle addition to water-based nanofluids (conventional nanofluids). It was found that the specific heat capacity of conventional nanofluids increases with an increase in temperature while it decreases with an increase in the volume fraction of nanoparticles. Less attention was given to the effect of size of nanoparticles on the specific heat capacity of nanofluids in the literature. All the developed correlations, based on the experimental results, were only a function of temperature and volume concentration. A new correlation was developed in this investigation based on the available experimental data for Al_2O_3–water nanofluids as a function of temperature, volume fraction, and the size of the nanoparticles.

Controversial results were reported for the specific heat capacity of molten salt-based nanofluids. A number of studies had claimed an enhancement in the specific heat capacity of molten slat-based nanofluids compared with the base mixture using only 1% concentration of nanoparticles by weight. However, other studies claimed that the specific heat capacity of nanofluids decreases with an increase in the volume fraction of nanoparticles. Disagreement was also found in the results

regarding the effect of the size of the nanoparticles on the specific heat capacity. More experimental results should be conducted to study the effect of volume fraction and the size of the nanoparticles on the specific heat capacity of molten salt-based nanofluids and consequently to explain the anomalous behavior of molten salt nanofluids.

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