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Simulation study of anomalous thermal properties of molten nitrate salt

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ABSTRACT

We performed Molecular Dynamics (MD) simulations to study the mechanism of the specific heat enhancement in nitrate salt based nanofluids. 26.6% enhancement of specific heat capacity was observed by introducing nanoparticles into the salt system. Our simulations showed that the nanoparticles caused a layering effect in the adjacent region of the liquid molten salt. Hence we attribute the enhancement in the specific heat capacity of molten salts with the addition of nanoparticles to a previously undiscovered structural arrangement of salt atoms around the nanoparticles.

1. Introduction

Thermal energy storage (TES) materials are widely used in renewable electrical energy generating applications [1–5]. The most important property of these media in energy storage applications is the specific heat capacity, which determines how much heat can be stored in a certain amount of TES material. In order to enhance their storage capacity, as a TES material, molten salts are often doped with nanoparticles. By using this strategy the specific heat capacity can be increased up to 50% [6–10]. The physical reasons why this happens, however, are not clear yet and data gathered so far show that the classic thermal equilibrium model [11] cannot be used in this case. Moreover, the results available sometimes clash with each other [11,12], and do not allow to draw a conclusive theory explaining the specific heat enhancement [6,7]. None of these theories, however, is supported by concrete evidence either experimental or theoretical.

The present work is based on the MD simulation of $NaNO_3$ based nanomaterials, but by the analysis of the effect on the internal energy of the nanoparticles we draft general conclusions and explain why molten salt have this specific heat enhancement while other materials (e.g. water) does not. In this paper we use molecular dynamics (MD) simulation to support, for the first time, a theory that can explain the apparently contradictory behaviour of the experimental data. This theory is similar to Shin et al. [6] proposed that the salt layer at the surface of nanoparticles, but it differs because we used MD to support the existence of an ordering layer and drew our mechanism of the enhancement.

2. Methodology

In this work we use MD simulations to calculate the thermodynamic properties of nitrate salt at different nanoparticle (SiO_2) concentrations. Specific heat capacity is calculated based on energy fluctuations from the canonical ensemble [13]. The density distribution of salt atoms from the centre of the nanoparticle is analysed by calculating the number of atoms per unit volume, defined as number density (ND).

Before calculating the properties of salt-nanoparticle system, we calculate salt and nanoparticle separately. Simulations computing densities of liquid pure salt and nanofluids were performed in the isothermal-isobaric ensemble using the Nose-Hoover thermostat and barostat [14]. With proper density achieved, simulations were performed using the Nose-Hoover thermostat in the canonical ensemble (NVT) [15].

Buckingham potential with Coulombic interactions was applied as force field for molten salt in this study:

$$v = A_{ij} e^{-\frac{r_{ij}}{\rho_{ij}}} - \frac{C_{ij}}{r^6} \tag{1}$$

where *v* is the interaction energy, *r* is the distance between site *i* and *j*. q is the charge of the atom at site *i* or *j*.

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The parameters in this study are given in Tables 1 and 2. Using these parameters reasonable results in computing thermal physical properties of nitrate salt was achieved in Jayaraman's study [16]. SPC water model was used to in water based nanofluids simulations.

Particle-particle-particle-mesh (pppm) [17] was used for coulombic interactions with an accuracy of 10^{-4}. To verify the physical properties presented by the potential and parameters, density and specific heat capacity were measured. The maximum deviation of the computed density differs by 2.63% from the reference value [18]. In our simulations, the specific heat capacity of $NaNO_3$ was fluctuating around the value of 1.5 $J\,K^{-1}\,g^{-1}$ when the relative deviation was less than 10% comparing to experimental results. The specific heat capacity of SiO_2 in simulations was 1.0 which was slightly over predicted comparing to the experimental value (0.85 $J\,K^{-1}\,g^{-1}$ at 300 K), but 15% deviation for MD simulation is also acceptable.

3. Results and discussion

Since the enhancement of specific heat capacity only happens in nanofluids, it is reasonable to believe it is affected by the size of particles and occurred at the surface of particles. Therefore, in our simulations we introduced SiO_2 nanoparticles with 1 nm diameter to increase the surface area of nanoparticles and the contact surface of salt and nanoparticles in order to maximize the enhancement.

The specific heat capacities of four systems containing different mass fraction of nanoparticles were computed and compared with that of the value calculated from the thermal equilibrium model [11] which are shown in Fig. 1. The theoretical value was calculated from the thermal equilibrium model [11]. Because the specific heat capacity of nanoparticles is lower than that of base fluids, the theoretical value showed decrease along with the increasing of nanoparticles. The deviation of simulation results are less than ±0.2. In our simulations, the specific heat capacity keeps increasing when more nanoparticles were introduced (Fig. 1A). In the system that contained 14% nanoparticles, the specific heat capacity increased to 1.79 $J\,K^{-1}\,g^{-1}$. This contradicts the results calculated from the thermal equilibrium model [11]. In the model, the specific heat capacity of the mixture decreased along with the increase of nanoparticles. When 14% nanoparticles were added in the system, the simulation results were 26.95% higher than in the thermal equilibrium model.

Similar results of enhancement in specific heat capacity were observed in our experiments. The specific heat capacity of the $NaNO_3$ was enhanced by introducing SiO_2 nanoparticles in different diameters. The specific heat capacity was enhanced by 15% in the nanofluid with 2% nanoparticles.

On the other hand, the specific heat capacity of water based nanofluids (Fig. 1B) did not gain any enhancement with the introduction of nanoparticles in our simulations. On the contrary the specific heat capacity of water decreased with the increase of SiO_2 particle fraction, which is in good agreement with the equilibrium mixing theory.

In the following section, effect of nanoparticles on the internal energy is analysed in order to explain why $NaNO_3$ behaves differently than water.

Table 1
Intermolecular parameters for the sodium nitrate and silica force field in this study.[a]

Atom	q_i (e)	A_{ij}(kcal mol^{-1})	ρ (Å)	C_{ij} (kcal mol^{-1} Å^6)
N	0.95	33,652.75	0.2646	259.1
Na	1	9778.06	0.3170	24.18
O (In $NaNO_3$)	−0.65	62,142.9	0.2392	259.4
O (In SiO_2)	−0.955209	15,170.70	0.386	617.24
Si	1.910418	72,460.64	0.351	14,415.29

[a] For the Buckingham potential (1), the cross terms were computed using the following mixing rules: $A_{ij} = (A_{ii}A_{jj})^{1/2}$, $C_{ij} = (C_{ii}C_{jj})^{1/2}$, and $(1/\rho_{ii} + 1/\rho_{jj})/2$.

Table 2
Intramolecular parameters for sodium nitrate.[b]

Atom		
N–O	k_b (kcal mol^{-1} $Å^{-2}$) = 525.0	$r_0(Å) = 1.2676$
N–O–O	k_θ (kcal mol^{-1} rad^{-2}) = 105.0	θ_0(deg) = 120.0
N–O–O–O	k_ψ (kcal mol^{-1} rad^{-2}) = 60	ψ_0(deg) = 0.00

[b] The flexible nitrate intramolecular parameters consist of bonds computed as $V_b = k_b(r - r_0)^2$, angles computed as $V_\theta = k_\theta(\theta - \theta_0)^2$, and an improper function of the form $V_\psi = k_\psi(\psi - \psi_0)^2$ to keep the nitrate species planar.

Fig. 2 demonstrates the difference of the distribution of the salt atoms in two systems. The RDF analysis in Fig. 2A indicates that without nanoparticles, the distance between a pair of nitrogen and sodium atom is greater than 2.43 Å because g(r) is zero when r< 2.43 Å. The first shell occurs at the distance of 3.33 Å where the nitrogen atoms are most likely to appear around a sodium atom. This information will become useful later on when we discuss the "compression" effect of the nanoparticles. Fig. 2B shows that in a molten salt with no nanoparticles system salt atoms are distributed evenly as expected. Fig. 2C, on the other hand, shows that the presence of the nanoparticle causes a separation between the anions and cations close to the surface of the nanoparticle. The first Na atom was detected at the radius of 5.1 Å and the peak value 1.39 was found at the radius of 7.65 Å. Number density of Na started to decrease and reach its lowest value, 0.899, at a radius of 9.35 Å before recovering to 1 at 12 Å. Nitrogen atoms kept increasing till reached their peak, 1.37, at the radius of 9.35 Å, where Na had its lowest value. The data for

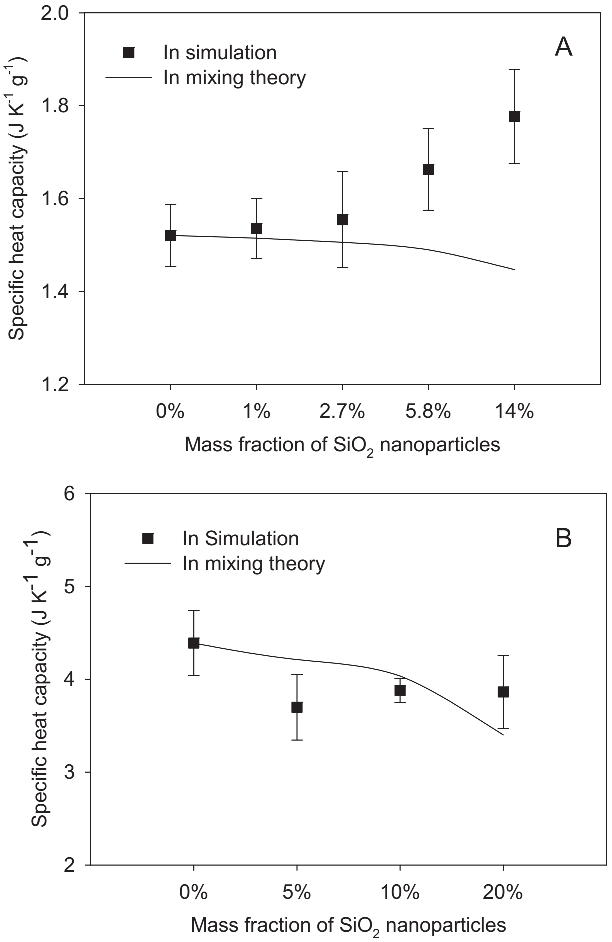

Fig. 1. Specific heat of nanofluids in simulations and in theory. A. $NaNO_3$ based nanofluids. B. Water based nanofluids.