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Effect of Al$_2$O$_3$ nanoparticle dispersion on the specific heat capacity of a eutectic binary nitrate salt for solar power applications

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Abstract: Molten salts can be used as heat transfer fluids or thermal storage materials in a concentrated solar power plant. Improving the thermal properties can influence the utilization efficiency of solar energy. In this study, the effect of doping eutectic binary salt solvent with Al$_2$O$_3$ nanoparticles on its specific heat capacity ($c_p$) was investigated. The effects of the mass fraction of nanoparticles on the $c_p$ of the composite nanofluid were analyzed, using both differential scanning calorimetry measurements and molecular dynamics simulations. The specific heat capacity of the nanocomposites was enhanced by increasing the nanoparticle concentration. The maximum enhancement was found to be 8.3%, at a nanoparticle concentration of 2.0%. A scanning electron microscope was used to analyze the material morphology. It was observed that special nanostructures were formed and the specific heat capacity of the nanocomposites was enhanced by increasing the quantity of nanostructures. Simulation results of $c_p$ agreed well with the experimental data, and the potential energy and interaction energy in the system were analyzed. The change in Coulombic energy contributed to most of the large change in $c_p$, which explains the discrepancy in values between conventional nanofluids and molten salt-based nanofluids.

Keywords: solar energy application; nanocomposite; specific heat capacity; molecular dynamics simulation; potential energy analysis
1. Introduction

The depletion of fossil fuels and the harmful gas emissions during the burning of fossil fuels compel the search for renewable and clean energy sources and higher efficiency of energy utilization [1–3]. To solve the energy crisis, some researchers focus on improving heat transfer efficiency via optimizing the heat transfer surface [4–7] while others tend to using high performance working media [8,9]. Meanwhile, the development of renewable energy was investigated. Solar energy is regarded as the best potential source to replace fossil fuels, with the average amount of energy transported to the earth as sunlight in one hour able to provide all of the energy currently consumed globally in one year [10]. A promising technology for the collection and use of solar energy is the concentrating solar power (CSP) system, which transforms solar energy to thermal energy with a heat-transfer fluid (HTF) [11]. Mahian et al.[12,13] used different working fluids in solar collectors and investigated the thermal efficiency. In solar collectors, lower specific heat capacity will induce a higher outlet temperature, increasing the solar energy utilization efficiency. However, solar energy is quite unsteady and unpredictable, since it varies from day to night, by cloud condition, and season. Hence, a working medium is needed to store the energy when it is available and then release it when there is insufficient sunlight. Considering the large amount of HTF and thermal energy storage (TES) materials required in a CSP plant, it is necessary to reduce the cost of these materials while improving their heat transfer and thermal storage performance. With thermal stability, comparable viscosity, and low vapor pressure at high temperature, various molten salts are used in modern CSP systems [14]. Solar salt, with a composition of 60% NaNO$_3$ and 40% KNO$_3$ by weight, was used in the Solar Two central receiver systems [15] and other solar plants [16]. Other molten salts are also being researched to improving the thermal performance [17–19].

However, these molten salts also have some disadvantages that limit the applicability of solar plants, for instance relatively low specific heat capacity and thermal conductivity [20]. Doping base fluids with nanosized particles to make nanofluids [21] is a potential way to improve their thermal properties, especially thermal conductivity [22]. Wen et al. [23] reviewed the heat transfer applications of nanofluids, including their formulations, influences on the effective thermal conductivity, and enhancement mechanisms. In previous research, various mechanisms have been identified that could enhance the effective thermal conductivities of these
materials, including the formulation of an interfacial layer, Brownian motion of the nanoparticles, ballistic transport of energy carriers, and structural effects. Most of the research has focused on thermal conductivity; however, the influence of nanoparticles on the specific heat capacity is still unclear [24].

Das et al. [25,26] investigated the specific heat capacity of nanofluids using a mixture of water and ethylene glycol as the base fluid. Silica, zinc oxide, and alumina nanoparticles were used and results indicated that the $c_p$ decreased with an increase in the nanoparticle concentration, but increased with increasing temperature. Similar results were found by Zhou et al. [27] with CuO nanofluids, Zhou and Ni [28] with Al$_2$O$_3$ nanofluids, and Elias et al. [29] with Al$_2$O$_3$ nanofluids. It seems that for conventional nanofluids (those with water, oil, ethylene glycol, or alcohol as the base fluid), the specific heat capacity is reduced by doping with nanoparticles. However, with molten salt or an ionic liquid as the base fluid, the influence of adding nanoparticles had the opposite effect. He et al. [30] prepared a carbonate salt/carbon nanomaterial composite to enhance the performance of a high-temperature salt. Both the specific heat capacity and thermal conductivity were significantly enhanced. Ding et al. [31] prepared a mixture of solar salt and nanoparticles by mechanic grinding and mixing. An enhancement of 10.48% in the specific heat capacity was obtained by adding CuO nanoparticles up to a mass concentration of 0.1%. Beyond this concentration, however, the enhancement worsened, and the specific heat capacity deteriorated at a concentration of 1.5%. Ho and Pan [32] formulated the Hitec-based Al$_2$O$_3$ nanocomposite in a specially designed rid at high temperature. They studied the effects of nanoparticle concentration on the specific heat capacities of nanocomposites and found that the optimal concentration was 0.063% with an enhancement of 20%. Jo and Banerjee [33,34] investigated the influence of graphite and multi-walled carbon nanotubes (MCNT) on the specific heat capacity of a carbonate mixed salt. An enhancement greater than 20% was obtained, and molecular dynamics simulations (MDS) were carried out to better understand the tremendous improvement. Shin et al. [35–39] performed a series investigation on carbonate salt-based SiO$_2$ nanocomposites. The enhancement in the specific heat capacity varied from 5% to 30%, and they proposed three models to explain the enhancement: (1) a higher $c_p$ for the silica nanoparticles than that of the bulk material; (2) solid-fluid interaction energy; and (3) a semi-solid layer formulation of liquid molecules surrounding the nanoparticles. Lu et al. [40] and Schuller et al. [41] prepared solar salt-based Al$_2$O$_3$ nanocomposites using a similar method, but obtained contrary results. The former
showed a decrease in the $c_p$, while in the latter it was enhanced 30.6%.

Though several studies have reported increased specific heat capacity, the rules and mechanisms involved for this increase in molten salts with nanoparticle doping are still insufficient. Most explanations about the significant enhancement of $c_p$ were based on some assumptions. In the present work, different mass fractions of solar salt-based nanofluids were investigated using experimental measurements and simulations. The nanomaterials were prepared by a dissolution method, and the specific heat capacity was measured by a differential scanning calorimeter (DSC) using the sapphire method. Material morphology analysis was conducted by a scanning electron microscope. The effects of nanoparticles on the potential energy were then analyzed by molecular dynamics simulations.

2. Experiment

2.1 Nanocomposite synthesis

In this study, we used the liquid solution method proposed by Shin et al. [36] to formulate the nanocomposites. Sodium nitrate and potassium nitrate were procured from Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd., both with purities above 99.0%. Al$_2$O$_3$ nanoparticles were purchased from Beijing Dk Nanotechnology Co. Ltd. The average diameter was about 20 nm and the purity was 99.99%. The procedure followed for obtaining the molten salt nanomaterial is illustrated in figure 1. Initially, 5 mg of Al$_2$O$_3$ nanoparticles were added to 20 mL of deionized water, which was then stirred for 20 min to form a suspension. Then, the suspension was sonicated for 60 min in an ultrasonicator (PS-100A, Jieken Ultrasonic Cleaner Limited, China) at a frequency of 40 kHz to ensure good dispersion and to minimize the potential agglomeration of nanoparticles. After that, different weights of the solar salt were dissolved in the suspension, so that the mass fraction of nanoparticles varied from 0.5% to 2.0%. The mixture was ultrasonicated for another 60 min to guarantee uniformity of the mixture. After sonication, the solution was then heated in a vacuum drying oven at atmospheric pressure with a temperature setting of 110 °C, according to the research of Jo [34] that evaporation temperature has little effect on the results. It was heated for 7 hours to obtain the dehydrated salt, which was the testing material for the DSC. All powders were weighed using an electronic microbalance (Sartorius MC 21S). It should be noted that there is no dispersing agent used in the preparation procedure.
2.2 Measurement of specific heat capacity

The specific heat capacities of the samples were measured based on the sapphire method using a DSC (204F1, NETZSCH). Aluminum pans were used to contain the samples, and the sample masses ranged from 5 mg to 15 mg. To protect the instrument from potential damage, the aluminum pans were covered with pierced lids. In the sapphire method, the heat flow through an empty pan, an aluminum pan with sapphire, and an aluminum pan with a prepared sample is measured. Then, using the three results and the specific heat capacity of sapphire, the specific heat capacity of each sample is calculated. The samples were heated to 50 °C and maintained at this temperature for 5 min to stabilize the calorimeter signal. A ramping rate of 20 °C/min was then applied, with the end temperature set to 450 °C. The sample was maintained at 450 °C for 5 min to ensure signal stability. Each sample was measured 3 times following the same procedure.

2.3 Uncertainty analysis

Uncertainties in the experimental results are dependent on the measurement deviations for each of the parameters, including mass and heat flow. The specific heat capacity was determined by Equation (1):

\[ c_{p,s} = c_{p,sapp} \cdot \frac{\Delta q_s \cdot m_{sapp}}{\Delta q_{sapp} \cdot m_s} \]  \hspace{1cm} (1)

where \( c_p \) is the specific heat capacity, \( q \) is the heat flow, \( m \) is the weight, and the subscripts \( s \) and \( sapp \) denote sample and sapphire. Taking \( f \) as a function of several independent parameters \( f_i \), and each uncertainty as \( \Delta f_i \), then the uncertainty of the experiment can be expressed as:

\[ d(\ln f) = \sum_{i=1}^{n} \left| \frac{\partial \ln f}{\partial f_i} \right| \Delta f_i \] \hspace{1cm} (2)

The accuracy of the electronic balance was ±0.005 mg, and the accuracy of the heat flow measurement was ±0.1 µW. Hence, the maximum measurement uncertainty of the specific heat capacity was estimated to be 2.4%.
3. Molecular dynamics simulations

Molecular dynamics (MD) simulations were performed to explore interactions between the nanoparticles and solvent molecules using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package. Initially, one \( \text{Al}_2\text{O}_3 \) nanoparticle fixed with a diameter of 2 nm was placed in the center of the simulation box and the solar salt molecules were placed randomly in the box, as shown in figure 2. The length of the simulation box was varied to adjust the nanoparticle mass concentration from 0% to 2.0%.

The Lennard-Jones (L-J) potential with long-range Coulombic force was employed to calculate the interaction between two non-bonded atoms, as shown in Equation (3), where \( E(r) \) is the potential of the two atoms, \( r \) is their distance from each other, \( q_i \) and \( q_j \) are the charges on atoms i and j, respectively, \( \epsilon \) is the potential well depth, and \( \sigma \) is the finite distance at which the inter-particle potential is zero. The L-J parameters between different atomic species were calculated by the Berthlot mixing rule \([42]\), as shown in Equation (4). In addition, bond stretching, bond bending, and torsion were considered for the bonded interactions, as shown in Equation (5), where \( r \) is bond length, \( \theta \) is bond angle, \( \phi \) is torsional angle, \( k_s \), \( k_b \), \( k_t \) are stretching, bending and torsional constants, respectively. All parameters used for the different atoms in the MD simulation are listed in Table 1.

\[
E(r) = \frac{q_i q_j}{r} + 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]
\]  
(3)

\[
\epsilon_{i,j} = \sqrt{\epsilon_i \cdot \epsilon_j}, \quad \sigma_{i,j} = \frac{(\sigma_i + \sigma_j)}{2}
\]  
(4)

\[
E = k_s \cdot (r - r_0)^2 + k_b \cdot (\theta - \theta_0) + k_t \cdot (1 + d \cdot \cos(n\phi))
\]  
(5)

Since the solar salt molecules were randomly placed in the simulation box, it is highly possible that there would be overlapping atoms, which would result in non-physical interactions. Hence, an energy minimization step was implemented to redistribute the atoms. During this step, the temperature of the system was reduced to zero K. Afterwards, a microcanonical ensemble was used to perform the relaxation procedure. Subsequently, the system temperature was raised to 650 K. A canonical Nose-Hoover thermostat (NVT integration, with a constant number of atoms \( N \), volume of the system \( V \), and temperature \( T \) controlled through direct temperature scaling) was used for the temperature range from 650 to 800 K to obtain the specific
heat capacity of the system.

4. Results and Discussion

4.1 Specific heat capacity results

The solar salt was doped with Al$_2$O$_3$ nanoparticles with an average diameter of 20 nm at mass fractions of 0.5%, 1.0%, 1.5%, and 2.0%. To guarantee the accuracy of the instrument, the melting temperature and enthalpy of Sn and Bi were measured and good agreement was shown with reference values, as shown in table 2.

Figure 3 shows the variations in the specific heat capacities of the base salt and nanocomposite mixtures in the full temperature range (80 °C to 400 °C). There are two peaks in the temperature range, at about 130 °C and 227 °C, which indicate the phase change temperatures. The peak at about 130 °C was formed by the solid-solid phase change of the eutectic salt and the peak at about 227 °C was formed by the solid-liquid phase change, agreeing with data from the literature [43] in which the respective peaks were at 130.4 °C and 224.8 °C. The specific heat capacity of the base salt in the liquid phase had an average value of 1.56 J/(g·K), showing a good agreement with values in the literature of 1.50 to 1.53 J/(g·K) [44], a less than 5% error. It also can be seen that the specific heat capacities of the samples changed only slightly with temperature, indicating that temperature does not substantially affect the specific heat capacities of these samples. In other words, the specific heat capacity is nearly independent of temperature. Meanwhile, we can see that with an increase in the mass fraction of the Al$_2$O$_3$ nanoparticles, the specific heat capacity of the samples increased.

Thermal energy storage (TES) capacity is an important parameter for TES systems, since it influences the scope of the system and the operating cost. The TES capacity (Q) was calculated as below.

$$ Q = \int_{260^\circ C}^{400^\circ C} \frac{h(T)\,dT}{mdT/dt} $$

(6)

where $h$ is the heat flow, $T$ is the working temperature, $m$ is the weight of the sample, and $dT/dt$ is the heating rate. The total Q for pure base salt and after adding 0.5, 1.0, 1.5, and 2.0 wt.% nanoparticles were 219.03, 223.01, 231.07, 233.84, and 236.32 kJ/kg in the working temperature range of 260–400 °C, respectively. This indicates that the Q value of the nanocomposite with ~2.0 wt.% nanoparticles has a maximum increase of 17.29 kJ/kg. Figure 4 plots Q versus temperature for pure base salt and after adding...
different amounts of nanoparticles. With increasing the nanoparticle mass fraction, the
TES capacity increases in the working temperature range of 260–400 °C.

Usually, the specific heat capacity of the mixture is calculated using a simple
mixing model. The mixing model is based on the assumption of thermal equilibrium
between the particles and fluid and can be expressed as:

$$c_{p,nf} = \frac{m_{np}c_{p,np} + m_sc_{p,s}}{m_{nf}}$$  \hspace{1cm} (7)

where $c_p$ is the specific heat capacity, $m$ is the mass, and the subscripts nf, np, and s
denote the property values of the nanofluid, nanoparticle, and salt, respectively. The
specific heat capacity of the base salt and Al$_2$O$_3$ particles are 1.56 J/(g·K) and 1.12
J/(g·K), respectively, as measured in present work. Figure 5 shows a comparison
between the experimental value and the value predicted by the simple mixing model.
The measured average specific heat capacity of the base salt and nanocomposites,
from lowest to highest concentration, were 1.56 J/(g·K), 1.59 J/(g·K), 1.65 J/(g·K),
1.67 J/(g·K), and 1.69 J/(g·K), respectively. This indicates that the specific heat
capacity of the nanocomposite with an Al$_2$O$_3$ particle concentration of about 2.0% by
weight has a maximum enhancement of about 8.3%. However, the prediction values
declined with an increase in the nanoparticle mass fraction, indicating that the
simple mixing model is not applicable in the evaluation of the specific heat capacity
of a nanocomposite.

4.2 Material Characterization

Since the specific heat capacity has a close relationship with the phase or
structure of the material, scanning electron microscope (SEM) (Quanta 200FEG) was
used to perform material characterization analyses. Figure 6 shows an SEM image of
the salt with various concentrations of nanoparticles after the DSC measurement. The
surface of the base salt was relatively smooth and had few visible structures. With the
addition of nanoparticles, some punctate and nubby microstructures appear (Figure 6
a). Adding more nanoparticles (Figure 6 b, c, and d) increases the quantity of these
microstructures and decreases the structure size. This kind of microstructure results in
an increase of the surface area. Due to the mismatch of vibrational density of states
between liquid and solid phase, there will be an interfacial thermal resistance, well
known as Kapitza resistance [45]. With the increase of the surface area, the total
interfacial thermal resistance will increase significantly [46,47], which will provide
additional thermal storage being responsible for enhancing the specific heat capacity.
4.3 Molecular dynamics simulations

To verify the accuracy of the MD simulations, the densities and $c_p$ values of the solar salt mixed with different mass concentrations of nanoparticles were calculated. Figure 7 shows the comparison of density results from the MD simulation system and theoretical calculation using Equation (8). Good agreement was obtained.

\[ \rho_{nf} = \varphi \rho_p + (1 - \varphi) \rho_f \]  
(8)

where $\varphi$ is the volume fraction of nanoparticles and the subscripts p and f denote the nanoparticles and fluid, respectively.

In figure 8, it can be seen that the total energy of the ensemble changes linearly with temperature for various nanoparticle mass concentrations, with an Adj. $R^2 > 0.998$. Hence, the $c_p$ of the solar salt-based nanofluid is almost constant in the temperature range of 650-800 K.

The specific heat capacity, $c_p$, is calculated as:

\[ c_p = \frac{\Delta E}{\Delta T \cdot V \cdot \rho} \]  
(9)

where $\Delta E$ is the energy change, $\Delta T$ is the temperature change, $V$ is the volume, and $\rho$ is the density of the ensemble. Figure 9 shows the experimental and simulated $c_p$ values with different nanoparticle mass concentrations. Acceptable agreement was obtained—for pure base salt, $c_p$ obtained from the MD simulation was 1.491 J/(g·K) with an error of about -4.42% compared with the experimental value of 1.56 J/(g·K).

The same trend with nanoparticle concentration was also obtained: $c_p$ increased with increasing nanoparticle mass concentration, and at 2.0 wt.% nanoparticles, the $c_p$ enhancements were 6.24% and 8.33%, respectively, for the simulation and experiment.

In order to explain this unusual enhancement of the $c_p$, we analyzed the energy components and interaction for each atomic type (figure 10) in the simulation. The energy of each atom can be divided into two parts: the kinetic energy ($E_{ke}$) and the potential energy ($E_{pe}$), as shown in Equation (10).

\[ E = E_{ke} + E_{pe} \]  
(10)

where the potential energy is composed of Van der Waals energy ($E_{vdw}$), Coulombic energy ($E_{coul}$), long-range k-space energy ($E_{long}$), and molecular energy ($E_{mol}$). From Figure 10, we can see that there was no significant change for $E_{ke}$, $E_{vdw}$, and $E_{long}$, while $E_{pe}$ increased with the nanoparticle mass concentration due to the increase of
E\text{coul} \text{ and } E\text{mol}. In other words, adding nanoparticles does not change the movement of molecules, the interaction potential between two atoms and the energy in k space. Figure 10 (b) shows the energy of three different intermolecular interactions in NO$_3^-$.

All of them change only slightly, indicating that the influence of added nanoparticles on the molecular structure of NO$_3^-$ is negligible. Hence, the slight increase in $E_{\text{mol}}$ per atom is due to the high molecular energy of Al$_2$O$_3$. Only the Coulombic energy change significantly for different nanoparticle mass fractions. Hence, the enhancement of $c_p$ is mainly due to the increase of the Coulombic energy, which can also explain the different effects on $c_p$ from adding nanoparticles to conventional base fluids and molten salts. Since there are more ions in molten salt, the influence of the Coulombic force is more significant.

**Conclusion**

In this study, the specific heat capacities of a binary nitrate salt and nanocomposites with different mass fractions of added nanoparticles (0, 0.5, 1.0, 1.5, and 2.0 wt.%, respectively) were investigated. The nanocomposites were synthesized using a solution method. DSC was employed to measure the specific heat capacity. Results show that the enhancement of the specific heat capacity of nanocomposites ranges from 1.9% to 8.3% with an increase in the mass fraction of added nanoparticles. The simple mixing model failed to predict the specific heat capacity of the molten salt-based nanofluids. Material characterization analyses were carried out using SEM. From the SEM images, we can see the formulation of punctate or nubby nanostructures, which may induce the enhancement of specific heat capacity through the enlarged specific surface area. The influence of nanoparticles on the energy components of each atomic type was analyzed by molecular dynamics simulations. Results indicate that the change in Coulombic energy per atom contributes the greatest portion of the enhanced $c_p$.

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Fig. 7 Comparison between simulations and theoretical calculations of the densities of a solar salt mixed with nanoparticles

Fig. 8 Total energy of the ensemble versus temperature: (a) 0.5 wt.%,(b) 1.0 wt.%3,(c) 1.5 wt.%,(d) 2.0 wt.%

Fig. 9 Experimental and simulated c_p values with different nanoparticle mass concentrations in the salts

Fig. 10 Potential and interaction energy analysis in the nanofluid system at 650 K
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Fig. 2 Simulation domain showing an Al$_2$O$_3$ nanoparticle surrounded by solar salt molecules
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Fig. 4 Variation of TES capacity with temperature, for pure base salt and after adding different amounts of nanoparticles.
Fig. 5 Comparison of average experimental $c_p$ values and the values predicted by the simple mixing model.

<table>
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<th>$c_p$ (J/(g·K))</th>
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Fig. 6 SEM images of the salt with various nanoparticle concentrations after DSC measurement:

(a) 0.5 wt.%, (b) 1.0 wt.%, (c) 1.5 wt.%, and (d) 2.0 wt.%. 
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Table 1 Simulation parameters for the MD simulation

<table>
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Table 2 Experimental validation

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<td>$m$</td>
<td>weight, kg</td>
<td></td>
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<tr>
<td>$E$</td>
<td>potential energy, J</td>
<td></td>
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<tr>
<td>$r$</td>
<td>distance between two atoms, Å</td>
<td></td>
</tr>
<tr>
<td>$q$</td>
<td>charge of atom, C</td>
<td></td>
</tr>
<tr>
<td>$k$</td>
<td>constant</td>
<td></td>
</tr>
<tr>
<td>$d$</td>
<td>sign convention constant</td>
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</tr>
<tr>
<td>$T$</td>
<td>temperature, K</td>
<td></td>
</tr>
<tr>
<td>$V$</td>
<td>volume, m$^3$</td>
<td></td>
</tr>
<tr>
<td>$Q$</td>
<td>thermal energy storage capacity, J/g</td>
<td></td>
</tr>
<tr>
<td>$h$</td>
<td>heat flow, mW/mg</td>
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**Greek symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
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<tbody>
<tr>
<td>$\varepsilon$</td>
<td>potential well depth, kcal/mol</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>finite distance for zero inter-particle potential, Å</td>
</tr>
<tr>
<td>$\theta$</td>
<td>angle value, degrees</td>
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<tr>
<td>$\varphi$</td>
<td>volume fraction, -</td>
</tr>
<tr>
<td>$\phi$</td>
<td>torsional angle, degrees</td>
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<tr>
<td>$\rho$</td>
<td>density, g/cm$^3$</td>
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**Subscripts**

<table>
<thead>
<tr>
<th>Subscript</th>
<th>Meaning</th>
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<tr>
<td>s</td>
<td>sample</td>
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<tr>
<td>sapp</td>
<td>sapphire</td>
</tr>
<tr>
<td>b</td>
<td>bending</td>
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<tr>
<td>t</td>
<td>torsional</td>
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