Encapsulated Nanoparticle Synthesis and Characterization for Improved Storage Fluids

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ENCAPSULATED NANOPARTICLE SYNTHESIS AND CHARACTERIZATION FOR IMPROVED STORAGE FLUIDS

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Abstract

Nanoparticles are typically composed of 50–500 atoms and exhibit properties that are significantly different from the properties of larger, macroscale particles that have the same composition. The addition of these particles to traditional fluids may improve the fluids' thermophysical properties. As an example, the addition of a nanoparticle or set of nanoparticles to a storage fluid may double its heat capacity. This increase in heat capacity would allow a sensible thermal energy storage system to store the same amount of thermal energy in half the amount of storage fluid. The benefit is lower costs for the storage fluid and the storage tanks, resulting in lower-cost electricity. The goal of this long-term research is to create a new class of fluids that enable concentrating solar power plants to operate with greater efficiency and lower electricity costs. Initial research on this topic developed molecular dynamic models that predicted the energy states and transition temperatures for these particles. Recent research has extended the modeling work, along with initiating the synthesis and characterization of bare metal nanoparticles and metal nanoparticles that are encapsulated with inert silica coatings. These particles possess properties that make them excellent candidates for enhancing the heat capacity of storage fluids.

Keywords: nanofluids, nanoclusters, heat capacity, molecular dynamics modeling, chemical synthesis

1. Introduction

Concentrating solar power (CSP) technologies represent a clear means for providing significant, utility-scale renewable electricity generation in the United States, Europe, and North Africa. In addition, commercial power plants with thermal energy storage (TES) are able to meet the intermediate-load profile with dispatchable power, a benefit that has high value to the power utilities. Cost analysis shows that improvements in plant thermodynamic efficiency and reduced capital costs will help CSP technologies meet their long-term cost goals. Meeting these goals will result in continued penetration of CSP technologies into utility-scale power markets.

Improving the properties of heat transfer and storage fluids is a important step in achieving these goals. The current state-of-the-art heat-transfer fluid (HTF) for parabolic trough power plants is a binary eutectic mixture of biphenyl and diphenyl oxide [1]. This HTF has a low freezing point (12°C) and is thermally stable to 393°C. At higher temperatures, the rates of several degradation reactions become excessively high and result in degradation of the HTF. The current state-of-the-art storage fluid is the eutectic mixture of $NaNO_3$ and KNO_3. The sensible enthalpy of this fluid is used to store and release thermal energy as it is cycled between high- and low-temperature storage tanks.

The 50-MW Andasol parabolic trough power plant in Spain uses this system to provide 7 hours of TES. New HTFs that possess a wide liquid temperature range will improve the thermodynamic efficiency of new parabolic trough power plants and reduce capital costs by decreasing the required storage inventory. Storage fluids that possess greater heat capacities will reduce the required storage inventory and lower plant capital cost. These material improvements are essential for improving the market competitiveness of both parabolic trough and power tower technologies.

2. Background

Nanoscale particles are being considered as additives to heat-transfer and storage fluids to improve the thermophysical properties of the fluids. Solids that contain nanoscale pore volumes filled with fluid are also being considered for storage applications. The nanoscale dimensional range is defined to be from 1 to 100 nanometers (nm) [2]. In some cases, this requirement applies to only two of the three object dimensions. Solid particles or fluid volumes within this size range typically contain 50 to 500 atoms and may exhibit properties that are different from their counterpart macroscale materials. Macroscale material particles exhibit physical properties (i.e., melting point, heat capacity) that are independent of their size. Nanoscale particles or fluid volumes have physical properties that vary significantly from those of their macroscale counterparts; and in addition, they also vary depending on the size of the nanoparticle. This effect is due to the relatively high proportion of atoms at the surface relative to those that are in the bulk of the particle. There are many examples of changes in physical properties of materials in the nanoscale size range. Copper nanoparticles smaller than 50 nm lack the malleability and ductility of macroscale copper. This effect is because the ductile behavior of macroscale copper is due to movement of atoms on a scale greater than 50 nm. In general, melting points and other phase transitions occur at different temperatures in nanoscale particles compared to those of the macroscale material.

Nanoparticles dispersed in fluids often form stable suspensions. The stability of these suspensions is due to the strength of the interaction of the nanoparticle surface with the fluid or solvent molecules. Because of the nanoparticle's high ratio of surface area to volume, the particle-fluid forces are strong enough to overcome settling forces, which are due to the density difference between the particle and fluid. This effect creates an opportunity for generating a class of fluids with improved physical properties. To aid this effect, methods are used in preparing nanofluids to ensure proper dispersion of the particles [3]. Addition of surface activators or surfactants decreases the surface tension between at the particle-fluid interface. Control of the fluid pH determines the charge type and distribution at the interface, adding to its stability. Use of ultrasonic vibration during initial mixing helps disperse agglomerates and establishes a proper particle dispersion.

Fluids with suspended nanoparticles have the potential to improve several physical properties of the fluid. There is evidence that suppression of the freezing point of fluids may also be achieved with the use of nanoparticles [4]. The addition of nanoparticles with a distribution of phase transitions to a fluid may significantly increase the heat capacity of the fluid. This benefit is due to two characteristics of nanoparticles. First, the melting point of nanoparticles varies as a function of the number of atoms within the particle. Second, the melting transition occurs over a temperature range, instead of at a single temperature. These variations allow the phase-change enthalpy of the particles to contribute uniformly to the sensible enthalpy of the fluid. The addition of a nanocluster or set of nanoclusters to a storage fluid may increase its heat capacity by a factor of 2 to 3. This increase allows the plant to store the same amount of thermal energy in less storage fluid. The benefit is lower costs for the storage fluid and storage tanks, resulting in lower-cost electricity.

There are potential drawbacks in adding nanoparticles to fluids. Studies have shown that fluids with high particle loadings (> 7%) show a marked increase in fluid viscosity [5]. This increase would quickly negate any benefit resulting from an increase in fluid heat capacity. The current high cost of nanoparticles also discourages the use of the high particle loadings that may be required for improved fluid heat capacity.

3. Objectives

The objectives for this work period were to: 1) extend the molecular dynamics modeling results for aluminum nanoclusters, and 2) synthesize and characterize encapsulated nanoscale particles that have the potential to increase TES densities by a factor of two or more over the current storage fluids for CSP applications.

4. Approach

Our approach uses molecular dynamics modeling to predict nanoparticle compositions that will optimize the thermophysical properties of heat-transfer and storage fluids. To date, we have limited our investigations to improving the heat capacity of fluids using nanoparticles with varying phase-transition temperatures. In macroscale materials, the transition between solid and liquid phases is abrupt in the sense that there exists a well-defined phase-transition temperature. The melting process in bulk materials is characterized by a sharp peak in the heat capacity at the melting temperature due to the enthalpy of the phase transition. As dimensions shrink into the nanoscale size range, however, phase transitions become highly size dependent. In general, the melting points of small particles less than 100 nm deviate significantly from the bulk melting points due to the high surface-to-volume ratio of nanosystems [6].

A comparison of the behavior of macroscale and nanoscale materials is illustrated in Figure 1, which shows the heat capacities, C_p, and enthalpies, H, for a set of three phase transitions over the temperature range, ΔT. For the macroscale material, the heat capacities are sharp, indicating the narrow temperature range of the transitions. Their corresponding changes in enthalpies have a "step" behavior relative to the sensible enthalpy line. For the nanoscale material, the heat capacities have a broad base, indicating a phase transition that occurs over a wide temperature range. The combination of three of these phase transitions produces an enthalpy change that is better matched to the sensible enthalpy line. Because the enthalpy change is latent, the change in enthalpy over the temperature range, ΔT, is much greater than the sensible enthalpy.
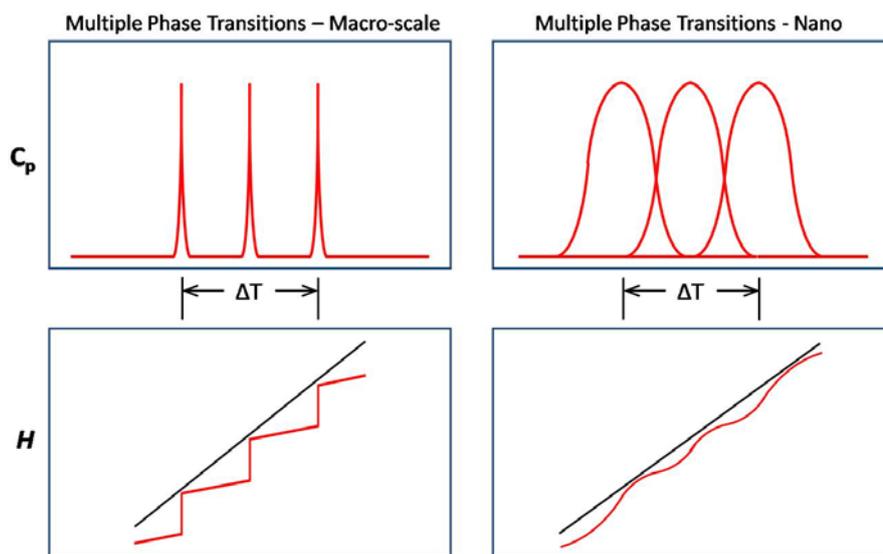

Figure 1. Heat capacities and enthalpy changes for sets of threemacro and nanoscale materials.

The size and shape of the heat capacity curve and its transition temperature depend on the number of atoms within the nanocluster particle. According to recent experiments, the addition or subtraction of just a single atom can make a dramatic difference in the melting properties [7,8]. The tunability of melting points, which is essential for the design of nanoscale storage fluids, is a genuine size effect of nanoscale particles. Figure 2 shows the variation of melting temperature with number of atoms within aluminum nanoparticles. The melting temperatures of these aluminum nanoparticles are up to 400°C less than that of macroscale aluminum.
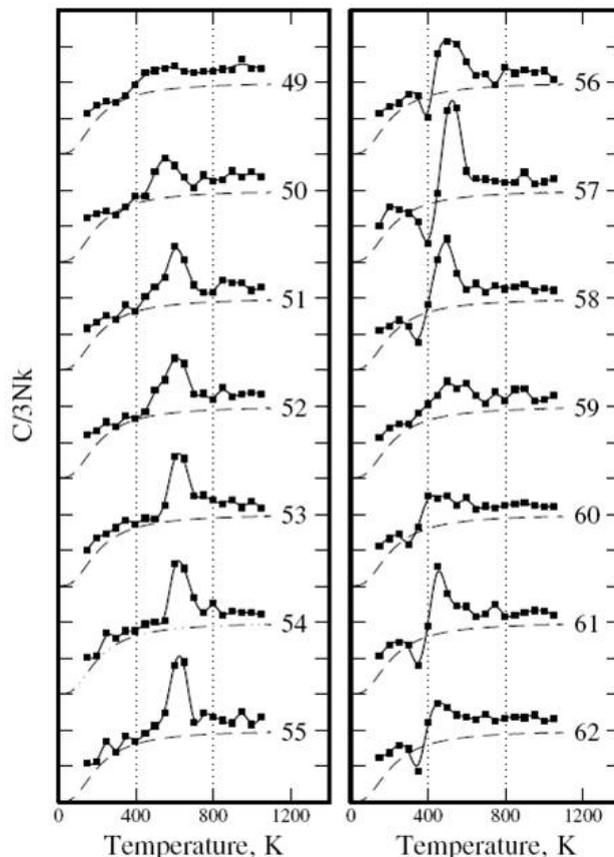

Figure 2. Variation of melting temperature with nanoparticle size for aluminum.

5. Results: Molecular Dynamics Modeling

We used molecular dynamics (MD) computer modeling to predict the energy states of stable aluminum nanoclusters and predict the transition enthalpy as a function of temperature for various aluminum nanoparticles. Figure 3 shows the heat capacities as functions of temperature for three aluminum clusters containing 55, 57 and 64 atoms. The broad peaks in heat capacities correspond to phase transitions that are shown under each graph. The black lines are experimental data and the red lines are the results from the MD model.

These three clusters undergo three types of melting behaviors. The first type is a simple melting transition that occurs from the solid-like to liquid-like phase as the temperature increases. This transition results in a peak in the heat capacity at the melting point. In the second type, a dip appears in the heat capacity at a temperature just below the melting point. Finally, the third type represents some aluminum nanoparticles that do not melt, even though the particles consist of a sufficiently large number of atoms, more than 60. In this case, the heat capacity increases gradually and does not show a pronounced peak.
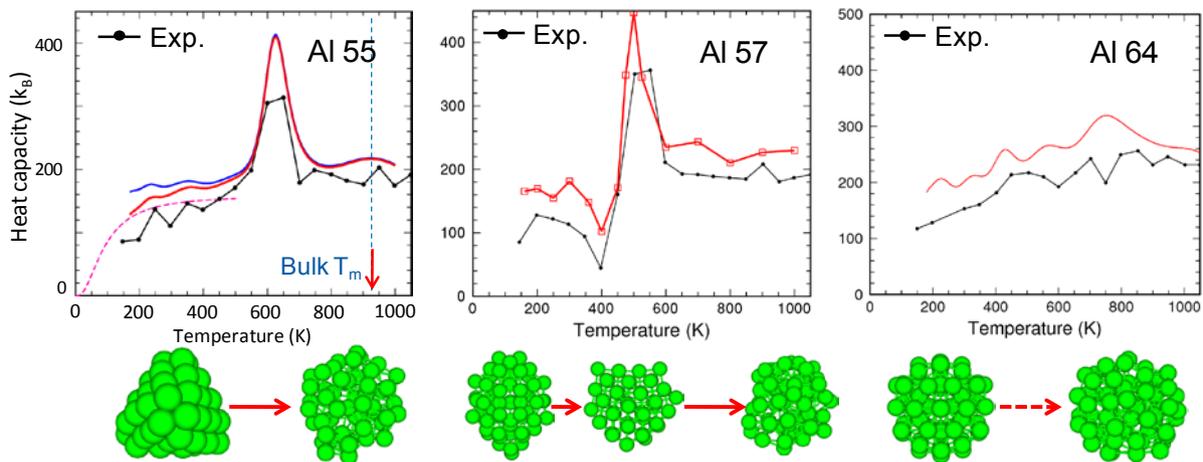
4

Figure 3. Variation of melting temperature with nanoparticle size for aluminum.

We performed MD simulations to elucidate the mechanism of the solid/liquid phase transition for these types of transitions. The melting points and enthalpies of nanoparticles depend on the inter-atomic potentials and geometry of nanoparticles. Therefore, a quantum description of inter-atomic forces and potential energy surface was imperative for the atomic-scale modeling of nanoscale melting. We performed long-term MD simulations at various constant temperatures ranging from 160 to 1200 K and calculated theoretical heat capacities in that temperature range. We found that the theoretical heat capacities agree well with the experimental results for the aluminum nanoclusters, including the three melting behaviors in Figure 3. These results demonstrate the predictive power of our theoretical methods.

5. Results: Particle Synthesis

Silver nanoparticles (AgNP) capped with cetyl-trimethyl-ammonium-bromide (CTAB) were synthesized by Burst's protocol [9]. In a typical reaction, 5 millimoles of CTAB were dissolved in 50 milliliters of nanopure water (maintained at 35ºC). To this, 0.5 millimole of $AgNO_3$ was added, yielding a white cloudy colored precipitate indicating the complexion of the CTAB with the metal salt. After running the reaction for 10 min, 0.5 millimole of $NaBH_4$ was added. The color of the white precipitate immediately turned black, indicating the formation of AgNP capped with CTAB. The reaction was allowed to run for 3 h and then stand overnight. The solution was centrifuged for 15 min at 4,500 rpm to remove the excess CTAB that settles as sediment, while the AgCTAB nanoparticles contained in the supernatant were decanted and stored under nitrogen atmosphere for further processing.

Transmission electron microscopy (TEM) was used to measure the nanoparticle core dimensions. Figure 4 shows the TEM micrograph for the above-synthesized AgCTAB nanoparticles. First, it can be clearly seen that the particles are very uniformly dispersed without any apparent aggregation. This indicates that the CTAB molecules strongly localize on individual nanoparticles and bind very effectively onto the Ag surfaces, thus forming a very efficient passivating layer on the particle surface that prevents agglomeration. Second, from the micrograph the size of AgNP can be estimated in the range of 7–10 nm with a modest amount of size variation.
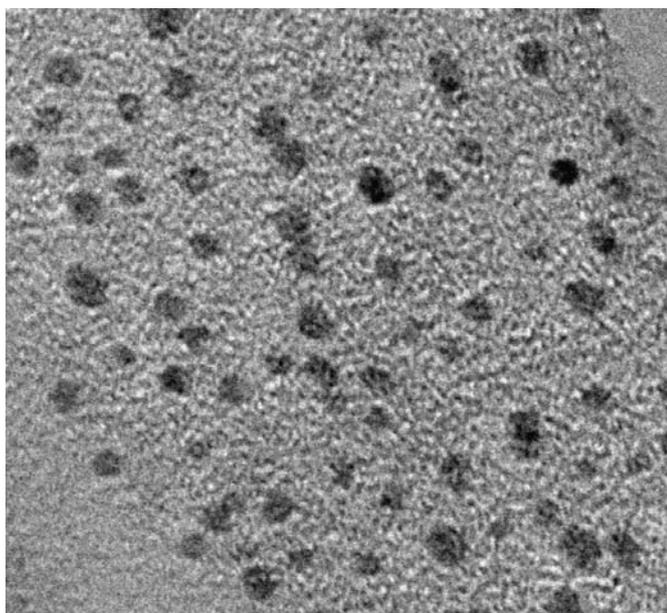
Figure 4. TEM micrograph of silver nanoparticles.

6. Results: Particle Encapsulation

 After synthesizing bare Ag nanoparticles, we synthesized Ag nanoparticles that were encapsulated with silica (SiO_2) coatings or shells. These particles were prepared by polymerizing the silica layer around the surface of Ag nanoparticles using a previously established sol gel process. TEM images of the particles at two magnifications are shown in Figure 5. It can be clearly observed that the mesoporous silica is coated very uniformly on the Ag surface. Note that for the present study, in spite of having numerous choices, CTAB was deliberately chosen as the capping agent for the nanoparticles. They can serve not only as the stabilizing surfactant for the nanoparticles in the aqueous phase, but also as the organic template for forming the mesoporous silica coating via base-catalyzed hydrolysis of tetraethyl-ortho-silicate (TEOS) and subsequent condensation of silica onto the surface of the CTAB molecules. From the micrograph, the thickness of the silica coating around the nanoparticle surface can be estimated to be about 15 nm. The thickness of the silica coating of this size is deliberately chosen to ensure that the particle core structure maintains its structural integrity during exposure to elevated temperatures. The mesoporous nature of the silica shell allows heat to enter and exit the nanoparticle ensemble, thus making it functional as a phase-change material.
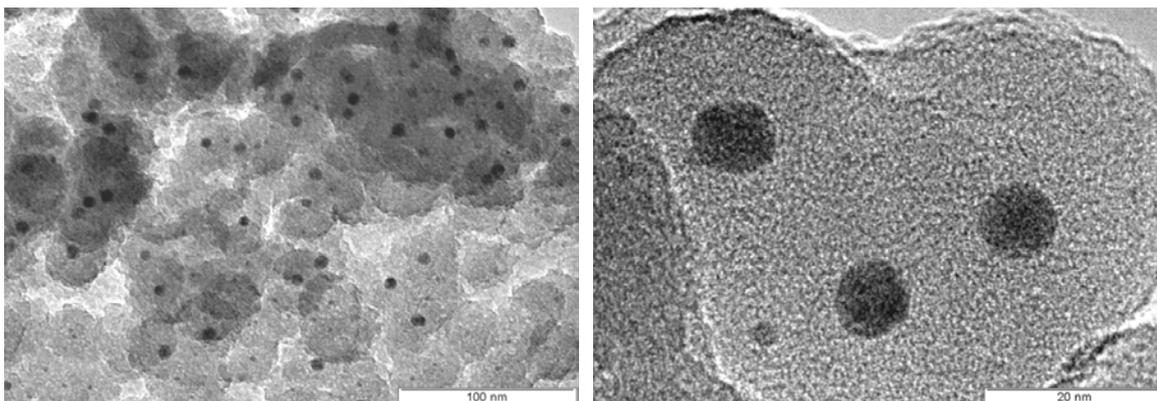

Figure 5. TEM images of silica-coated silver nanoparticles.

This work demonstrates that uniform nanoparticles can be synthesized and encapsulated with an inert shell. The shell will preserve the core particle as it undergoes phase transitions (melt-freeze) and prevents agglomeration of the core particles when they are in the liquid phase. These results represent the initial steps in developing a new class of storage fluids that possess enhanced thermophysical properties. The next steps will build on these results and use differential thermal analysis to observe melting transitions of the Ag particles over a temperature range that is expected to be significantly different from the melting point of macroscale Ag (962°C).

7. Future Work

The synthesis of encapsulated nanoparticles creates the opportunity for more research into the characterization of these particles. We will attempt to observe reversible phase transitions of the Ag cores. Reversible phase transitions were recently observed in nanoparticles with indium cores and silica shells [10]. The phase transitions of the indium cores were between 120° and 160°C, which are too low to be useful for CSP applications. These results, however, demonstrate the mechanism of this approach to enhance heat capacity.

We will also incorporate encapsulated nanoparticles into storage fluids to determine their effect on the thermophysical properties of the fluid. Past work has identified fluid molecule ordering at the fluid-particle interface [11]. The transition energies of this effect may be a mechanism for enhancing the fluid heat capacity. This fluid ordering at the interface may be a means to increase the heat capacity with particles that do not undergo explicit phase transitions. We will be investigating this approach, as well.

Acknowledgements

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