International Journal of Heat and Mass Transfer 66 (2013) 575–584

Contents lists available at ScienceDirect

International Journal of Heat and Mass Transfer

journal homepage: www.elsevier.com/locate/ijhmt

Molecular dynamics simulations of nano-encapsulated and nanoparticle-enhanced thermal energy storage phase change materials

Zhonghao Rao [a,b], Shuangfeng Wang [a,*], Feifei Peng [a]

[a] Key Laboratory of Enhanced Heat Transfer and Energy Conservation of the Ministry of Education, South China University of Technology, Guangzhou 510640, China
[b] School of Electric Power Engineering, China University of Mining and Technology, Xuzhou 221116, China

ARTICLE INFO

Article history:
Received 15 January 2013
Received in revised form 21 July 2013
Accepted 21 July 2013
Available online 15 August 2013

Keywords:
Thermal energy storage
Phase change material
Nano-encapsulated
Molecular dynamics simulations

ABSTRACT

The nano-encapsulated and nanoparticle-enhanced phase change materials (PCM) which can be used for thermal energy storage have attracted much attention in recent years. To understand the heat and mass transfer mechanisms of the nano-encapsulated and nanoparticle-enhanced PCM on the molecular and atomic scale, the molecular dynamics (MD) simulations were performed in the present paper. The nano-encapsulated PCM with different shell thicknesses were fabricated by using *n*-octadecane as core material and SiO_2 as shell material. The nanoparticle-enhanced PCM were formulated by mixing Al nanoparticles into *n*-nonadecane. The *n*-nonadecane, *n*-eicosane, *n*-heneicosane and *n*-docosane were used to build the pure PCM models as unencapsulated PCM systems for comparison. The results showed that the torsion and extension of the core material molecule chains could be restricted by excessive thick shell in the nano-encapsulated PCM systems. The mobility of the nanoparticle-enhanced PCM decreased with the increase of the diameter of added nanoparticles. Both excessive thick and thin shells were disadvantageous for encapsulated PCM. And the appropriate size of particle was very important for heat transfer enhancement of the nanoparticle-enhanced PCM. The MD simulations proposed herein can be helpful for the material design and performance optimization of thermal energy storage and transport PCM.

1. Introduction

With the continuous increasing pressure of energy shortage and environmental pollution, to reduce the mismatch between energy supply and its demand, energy storage and renewable technologies have received much attention in worldwide economic progress and industrialization. Various energy conservation forms have been developed for effective and efficient utilization of the energy source both in the energy storage and in the transporting process. Compared with those materials which have high energy density, the thermal energy storage materials are also very important for the capture and utilization of waste heat and recovering energy from low grade heat sources. As known thermal energy demands all over the world are essential especially for various forms of heating and cooling applications. For instance, in the United States the total thermal energy demand (33.5 EJ) in the temperature range from 0 °C to 260 °C in 2008 is about one third of the entire US demand and 55% of them come from the residential sector, 24% from the industrial and 21% from commercial sectors [1]. Among a variety of thermal energy demands, the storage of thermal energy including sensible and latent heat is of growing importance in recent years.

The use of phase change materials (PCM), which store thermal energy mainly in the form of latent heat, has been one of the most efficient methods to store thermal energy since the PCM provide higher heat storage capacity and more isothermal behaviors during phase transition compared to sensible heat storage [2]. In the past decades, the thermal energy storage PCM have been widely investigated and applied in many areas. To date many kinds of PCM which can be classified into organic, inorganic and eutectics are available for thermal energy storage in any required temperature range [3]. Most of organic PCM such as paraffin have advantages in non-corrosive and chemically stable, performance little or no sub-cooling in comparison to inorganic materials such as salt hydrate and metallic [4]. On the other hand, phase change temperature is a key factor for selecting suitable PCM. And 38% of the thermal energy below 260 °C in US, which was used for space heating and water heating in the residential and commercial sectors, has end-use temperatures of 40–60 °C [1]. Hence, the commercial paraffin, with a wide range of melting and solidification

* Corresponding author. Tel.: +86 20 22236929.
E-mail addresses: raozhonghao@cumt.edu.cn (Z. Rao), sfwang@scut.edu.cn (S. Wang).

0017-9310/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ijheatmasstransfer.2013.07.065

temperature and moderate thermal storage densities (200 kJ kg^{-1} or 150 MJ m^{-3}) [5], have been studied most as thermal energy storage PCM.

An undesirable property of paraffin-based PCM is their relatively low thermal conductivity, which lead to suppressing the energy charging and discharging rates, that heat transfer enhancement are required for extending their applications [6]. In order to overcome the disadvantages of paraffin-based PCM including low thermal conductivity, high change in volume on phase change and flammability, extensive investigations have been developed [7]. A novel encapsulation technology was recommended and confirmed effective. The paraffin is used as core materials and encapsulated into shell materials such as polymer to fabricate macro, micro and nano-encapsulated PCM [8]. The capsules mixed with carrier fluid and prepared as nanofluids or PCM slurries will significantly increase the heat transport capability [9]. In addition, the nanomaterials with high thermal conductivity such as alumina nanoparticles [10], copper nanoparticles [11], carbon nanofibers and nanotubes [12], exfoliated graphite nanoplatelets [13], also can be dispersed directly into paraffin to form nanocomposite PCM for enhancing the heat transfer. More than 30 review articles focusing on PCM including preparation, characterization and applications have been published during the last decade. The main research methods in the previous investigations for PCM contain experiment [4] and numerical calculation or simulation (mostly in macro perspective) [14,15]. Actually, as the thermal properties of PCM are influenced by experimental conditions in which some reported parameters of the similar PCM showed large difference. Sari and Karaipekli [16], Xia et al. [17] and Zhong et al. [18] all presented the study on thermal conductivity of paraffin/expanded graphite composite PCM. The thermal conductivity of the composite PCM with 2%, 4%, 7%, and 10% expanded graphite in Sari and Karaipekli [16] work is 0 W m^{-1} K^{-1}, 0.40 W m^{-1} K^{-1}, 0.52 W m^{-1} K^{-1}, 0.68 W m^{-1} K^{-1} and 0.82 W m^{-1} K^{-1}, while in Xia et al. [17] work, is about 0.50 W m^{-1} K^{-1}, 1.28 W m^{-1} K^{-1}, 3.03 W m^{-1} K^{-1} and 3.88 W m^{-1} K^{-1}, respectively. The reason which can be found in Zhong et al. [18] work is that the thermal conductivity of the composite PCM is affected by the bulk density of expanded graphite. Besides, as the unevenness of dispersion and instability during flow especially for nano-encapsulated and nanoparticle-enhanced PCM with tiny amount and in small-scale, accurately obtaining the thermal parameters of PCM is very important for efficient applications. Note that molecular dynamics (MD) simulation has become an important method in understanding the microscopic behaviors of various materials [19–21]. The MD simulation provides ultimate detail for addressing specific questions concerning inherent mechanism, often more easily than experiments on the actual system [22]. It is meaningful and necessary to use MD method for analyzing and predicting the thermal properties of PCM from molecular and atomic scale.

The paraffin-based thermal energy PCM usually consists of a mixture of mostly straight chain *n*-alkanes CH_3–$(CH_2)_n$–CH_3 [23]. Thus, in the MD simulation, the model of paraffin-based PCM system can be simplified as *n*-alkanes and their mixture. In our previous MD simulation work, the *n*-nonadecane was used as pure PCM and its phase transition behavior under high pressure was investigated [24]. The water/*n*-nonadecane models were used as PCM slurry and the melting behavior was described [25]. The melting behavior of encapsulated PCM, which was fabricated by using *n*-octadecane as core material and SiO_2 as shell material, with a diameter 5 nm under free and constrained conditions were also presented recently [26]. For the potential material design and performance optimization of nano-encapsulated and nanoparticle-enhanced PCM, in the present study, the MD modes of nano-PCM such as *n*-octadecane encapsulated with SiO_2 and *n*-nonadecane filled with Al nanoparticles are fabricated and discussed for further understanding the energy storage and heat transfer mechanisms. The investigation will contribute to the development and application of PCM for thermal energy storage and transport.

2. Models and methods

Fig. 1 displays the typical structures of the nano-encapsulated and nanoparticle-enhanced PCM. In the MD simulations, three types of PCM models including nano-encapsulated, pure alkane-based and nanoparticle-enhanced PCM systems were constructed to simplify the calculation, respectively. Three nano-encapsulated PCM systems were fabricated by using *n*-octadecane ($C_{18}H_{38}$) as core material and SiO_2 as shell material. The diameter of the nanocapsules was set as 4.2 nm and the thickness of the shell was set as 0.8 nm, 0.6 nm and 0.4 nm, respectively. The final configuration of the three nanocapsules all contained 17 *n*-octadecane molecules, while SiO_2 molecules, 657, 544 and 406, respectively. Then the nanocapsules were dispersed into water to form three types of nanofluids. Each nanofluid system contained 2706 H_2O molecules. And the total atom number of the three nano-encapsulated PCM systems is 11,041, 9750 and 9336, respectively. Before fabricating the nanoparticle-enhanced PCM systems, four pure PCM systems with amorphous structures were built. The pure PCM consists of *n*-nonadecane ($C_{19}H_{40}$), *n*-eicosane ($C_{20}H_{42}$), *n*-heneicosane ($C_{21}H_{44}$) and *n*-docosane ($C_{22}H_{46}$), respectively. The number of molecules in each pure PCM model is 20. The Al nanoparticles were mixed with *n*-nonadecane to fabricate the nanoparticle-enhanced PCM. Four nanoparticle-enhanced PCM systems were built and the diameter of the filled Al nanoparticles is 1 nm, 2 nm, 3 nm and 4 nm, respectively. And the corresponding atom number of Al is 43, 249, 887 and 1985, respectively. The number of *n*-nonadecane molecules in the four nanoparticle-enhanced PCM systems all set as 80. And the total atom number of the four nanoparticle-enhanced PCM systems is 4763, 4969, 5607 and 6705, respectively.

The calculations of the above mentioned models were carried out by using classical MD method. The condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) force field [27] were used to perform the calculation. Details of the potential employed in this work can be found in Ref. [42]. After a structure was built, the Smart Minimizer method, which starts with the steepest descent method, followed by the conjugate gradient method and ends with a Newton method, was used to refine the conformation. And then 100 ps in constant-pressure, constant-temperature (NPT) ensemble, followed by 100 ps in constant-volume, constant-temperature (NVT) ensemble were used to equilibrate the system. The energies fluctuating of one of a kind nano-encapsulated PCM model during minimization and relaxation process were shown in Fig. 2. The dynamic processes used for data analysis were performed in NPT ensemble after each system equilibrated. The time step all set as 1 fs in the dynamic processes. The Nosé method [28] and Berendsen method [29] were used for controlling temperature and pressure, respectively. The Atom based [30] and Eward [31] method were used to calculate the van der Waals and Coulomb interactions. The equation motion was integrated by using the Verlet velocity algorithm [32]. In our work, MD simulations were performed by using Amorphous and Discover program incorporated in the Materials Studio (Accelrys) [33].

3. Results and discussions

3.1. Self diffusion of the nano-encapsulated PCM

Self diffusion is one of the most important thermophysical properties that control mass-transfer phenomena and used for