International Conference on Applied Energy 2019
Aug 12-15, 2019, Västerås, Sweden
Paper ID: 238

MONTE CARLO SIMULATION STUDY ON THE COLLOIDAL STABILITY OF NANOPARTICLES IN MOLTEN SALTS

Feng Ji[1], Weilong Wang [2*], Juntong Xing[1], Jing Ding[2], Xiaolan Wei[3]

1 School of Intelligent Systems Engineering, Sun Yat-sen University, Guangzhou 510006, PR China

[2] School of Materials Science and Engineering, Sun Yat-sen University, Guangzhou 510275, PR China

[3] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China

ABSTRACT

Molten salt-based nanofluids have better thermal properties than pure molten salt due to dispersing nanoparticles. However, the aggregation of nanoparticle can waken heat transfer. In this paper, Kinetic Monte Carlo simulations based on the classical DLVO theory were carried out to predict the MgO nanoparticle size distribution suspending in the molten $NaNO_3$ with different initial particle diameters. The result suggests that nanoparticles with size of 10nm~30nm tend to form clusters and larger diameters such as 40nm and 50nm could lead to a more stable system for molten salt nanofluid.

Keywords: molten salt nanofluids, Kinetic Monte Carlo, aggregation and sedimentation, DLVO theory

NONMENCLATURE

k	*Boltzmann constant*
e	*Unit electronic charge*
ε	*Dielectric permittivity of the medium*
ε_0	*Dielectric permittivity of vacuum*
κ	*Debye Length*
A_H	*Hamaker constant*
Ψ_0	*Surface potential*
μ	*Viscosity of the molten salts*
ρ_b	*Density of the molten salts*
ρ_p	*Density of the nanoparticles*

INTRODUCTION

Molten salts are widely used in solar, nuclear and other high temperature systems as heat transfer and storage fluids. In Concentrated Solar Power plants, many different salts are selected, among these Nitrate salts are most used owing to its relatively low cost, high heat capacities and thermodynamically stable.

In 1995, Choi [1] added nanoparticles into the liquid and found the heat transfer performance of liquid improved a lot especially when the volume fraction of nanoparticles was at a low level (less than 0.01%). According to this phenomenon, more and more molten salt-based nanofluids are implemented in engineering currently. However colloidal aggregation may weaken the heat transfer performance of nanofluids, it is valuable to clear the mechanism of colloidal stability. Many experimental and numerical research have been conducted to study the aggregate kinetics of nanoparticles in water or ionic liquid and few in molten salts. In general perspective, the interaction forces between nanoparticles including van der Waals attraction and electrostatic repulsion are responsible for the colloidal stability of nanofluids. Different from the water based nanofluids, molten salt is a high temperature and high ion concentration system, due to strong Brownian motion and thin electric double layer, particles tend to aggregate in molten salts [2]. In this paper, MgO nanoparticles and $NaNO_3$ molten salt are selected as materials of nanofluid, and the effect of size of particle is discussed via Monte Carlo simulation.

* Corresponding author. Tel.: +86-020-3933-2320;
E-mail address: wwlong@mail.sysu.edu.cn

Selection and peer-review under responsibility of the scientific committee of the 11th Int. Conf. on Applied Energy (ICAE2019).

1. THE PHYSICAL MODEL

1.1 Interaction between nanoparticles

The behavior of aggregation and sedimentation of nanoparticles is the result of Brownian motion, DLVO interactions and some other forces.

2.1.1 van der Waals attraction

One of the most important interaction between MgO suspending nanoparticles is the van der Waals force of attraction, which has three components including Keesom, Debye and London forces. In present work, only London dispersion force is considered for its efficient description of colloidal system. For two spherical particles with size r_i and r_j, the van der Waals energy is calculated by [3]:

$$\phi_{vdW} = -\frac{A_H}{6}\left[\frac{2r_i r_j}{R^2-(r_i+r_j)^2}+\frac{2r_i r_j}{R^2-(r_i-r_j)^2}+\ln\frac{R^2-(r_i+r_j)^2}{R^2-(r_i-r_j)^2}\right] \quad (1)$$

where, A_H is the Hamaker constant, R is the center-to-center distance of MgO nanoparticles.

2.1.2 Electrostatic repulson

Another important interaction is Electrostatic repulsion. If metal oxides like TiO_2, Al_2O_3, MgO etc., are charged in molten salt or other aqueous medium, the electrostatic interaction between nanoparticles tend to repel each other and prevent aggregation, thereby ensuring the colloidal stability of the system. The force is also called electric double layer force, and it declines with the separation distance. Different pH conditions of medium may cause oxide surfaces become positive or negative charge, while the surfaces of MgO nanoparticles are positively charged at most pH values [4]. In present study, electrostatic energy between two sphere particles with size r is given by [5]:

$$\phi_{EDL} = 4\pi\varepsilon\varepsilon_0 R_R[\varphi_1\varphi_2\exp(-\kappa h)-\frac{1}{4}(\varphi_1^2+\varphi_2^2)\exp(-2\kappa h)] \quad (2)$$

where, $R_R=r_1r_2/(r_1+r_2)$, κ is the inverse Debye length, φ is the surface potential estimated by zeta potential, h is the surface distance between two particles.

2.1.3 DLVO theory

DLVO which was developed by Derjaguin, Landau, Verwey and Overbeek, can provide a reasonable description of nanoparticle aggregation. According to DLVO theory, van der Waals attraction force and electrostatic repulsion force are the dominant interactions between two nanoparticles in electrolyte solution, and total energy Φ_T is the sum of the two interactions [4]:

$$\Phi_{T,ij} = \phi_{vdW,ij} + \phi_{EDL,ij} \quad (3)$$

Usually, the former force is attractive and the latter is repulsive, however, this could change depending upon the properties of particle and based liquid. The interaction between particles is shown in Fig.1.

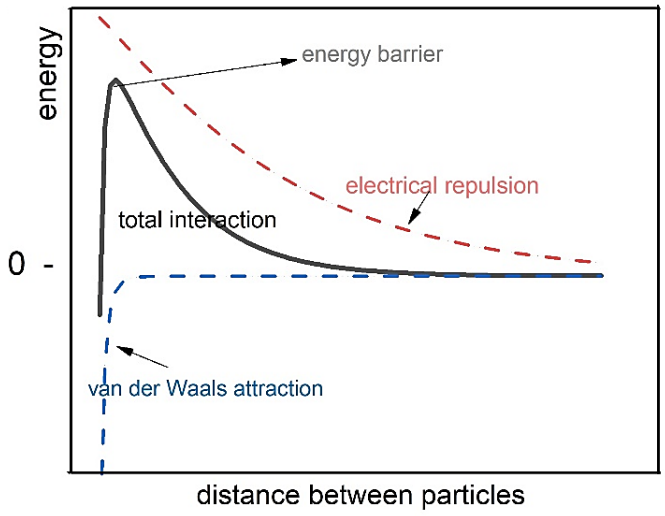

Fig.1. Interaction between particles according to DLVO theory

1.2 Aggregation and sedimentation kinetics

2.2.1 Sub-model for aggregation rate

Based on the Smouluchowsi model, the rate of collision between particles is proportional to the particle concentration. The number of collisions occurring between two particles per unit time in a unit volume is given by [3]:

$$N_{ij} = k_{ij} \bullet n_i \bullet n_j \quad (4)$$

Where n_i and n_j are the particle numbers with size i and j in the medium respectively. Many factors have influence on aggregation frequency like fluid properties and particle size. k_{ij} is the aggregation function expressed as [3]:

$$k_{ij} = \frac{\beta_{ij}}{W_{ij}} \tag{5}$$

In which β_{ij} represents the collision frequency dominated by Brownian motion, and can be described as [6]:

$$\beta_{ij} = \frac{2kT}{3\mu}(r_i + r_j)(\frac{1}{r_i} + \frac{1}{r_j}) \tag{6}$$

Where μ is the viscosity of the medium. Considering that the maximum potential Φ_{max} contributes the largest part to the stability ratio W_{ij} is simplified as a function of Debye length and barrier height rather than the entire DLVO profile [2]:

$$W_{ij} = \frac{1}{\kappa(r_i + r_j)} \exp(\Phi_{max} / kT) \tag{7}$$

If two particles are picked to aggregate, the mass of newly formed particle is linear sum of formers, and the effective diameter d_e is calculated as:

$$d_e = d_p \bullet n_P^{1/df} \tag{8}$$

Where n_p is number of particles in this group, and d_f is the fractal dimension for the specific agglomeration.

2.2.2 Sub-model for particle motion

The movement of nanoparticles in base fluids is the combination of Brownian motion, hydromechanics and gravity. In the present work, MgO nanoparticles are dispersing in molten salt which is a high temperature system, thus Brownian motion is an important part and the equation for particle is given by [7]:

$$\vec{F}_{B,i} = \vec{G_i}(6\pi\mu k_B T d_{p,i} / \Delta t)^{1/2} \tag{9}$$

where G_i is a random Gaussian vector with unit variance and zero mean, Δt is the time step. Apart from Brownian force, other type force like buoyancy, drag force and gravity are calculated by the following equations respectively [7]:

$$\vec{F}_{d,i} = -3\pi\mu d_{p,i}\vec{v}_i$$

$$\vec{F}_{buo,i} = \frac{\pi}{6}\rho_b d_{p,i}^3 \vec{g} \tag{10}$$

$$\vec{F}_{g,i} = \frac{\pi}{6}\rho_p {d_{p,i}}^3 \vec{g}$$

where g is the gravitational acceleration, ρ_p and ρ_b are the density of particle and base fluid. Total force works on the single particle is the sum of these forces. The motion of single particle satisfies Newton Second Law:

$$m_i \frac{d\vec{v}_i}{dt} = \vec{F}_{Total}, \frac{d\vec{x}_i}{dt} = \vec{v}_i \tag{11}$$

where x_i is the location of particle.

3. NUMERICAL MODEL

There are many effective methods to simulate the progress of nanoparticle aggregation such as Brownian dynamics (BD) and Molecular dynamics (MD) simulations. But these methods place a limit on number of particles, they will take too much computational cost when number of particles increases. While Kinetic Monte Carlo (KMC) provides a practical and efficient approach to simulate aggregation of lots particles in a domain, where each event has a probability quantified by the physical colloidal theory [8].

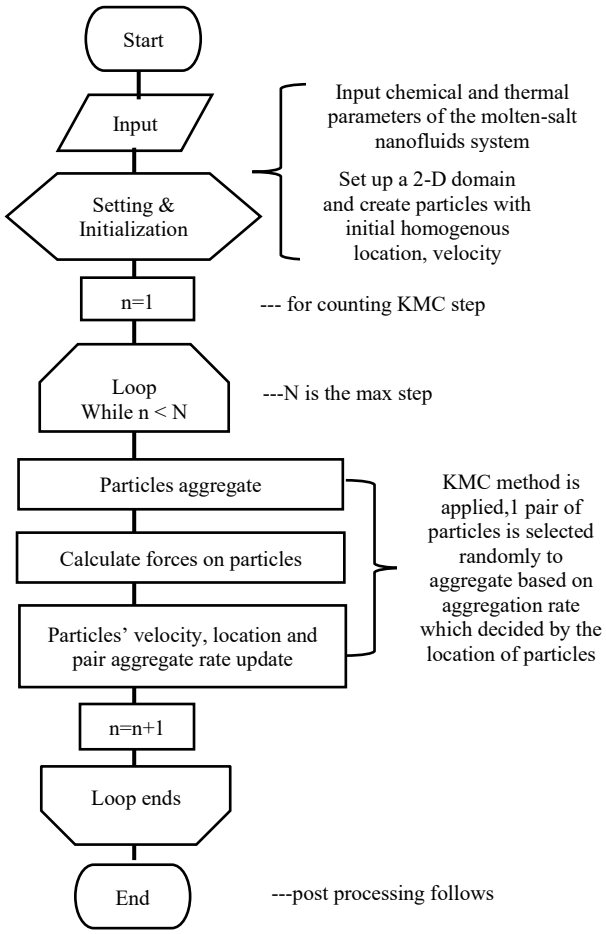

Fig.2. The flowchart of kinetic Monte Carlo simulation

In the present study, nanoparticle aggregation and sedimentation are investigated by KMC. 50 MgO nanoparticles with size ranging from 10nm to 50nm are homogenously dispersing in the cube domain, newly particle will be added if aggregation happens, the cube is expending to maintain the mass fraction of the system, and its volume can be calculated as [3]:

$$V = \frac{\rho_p}{C} \bullet \sum_{i=1}^{N} (\frac{4}{3}\pi \bullet r_i^3) \tag{12}$$

where C is the initial mass concentration of MgO in molten $NaNO_3$. Every pair of particles is likely to aggregate and time interval between aggregations is estimated based on average aggregation frequency function over all particle pairs [3]:

$$\Delta t = \frac{2}{C \bullet N \bullet < k_{ij} >} \tag{13}$$

The flowchart of present simulation is show in Fig.2.

4. RESULT AND DISCUSSION

Different sizes of MgO nanoparticle, which are initialized as 10nm, 20nm, 30nm, 40nm and 50nm, with the same weight fraction dispersed in 550K $NaNO_3$ molten salts are studied in this work. Mean diameter distribution after 5 times simulations for each size is presented in Fig.3.

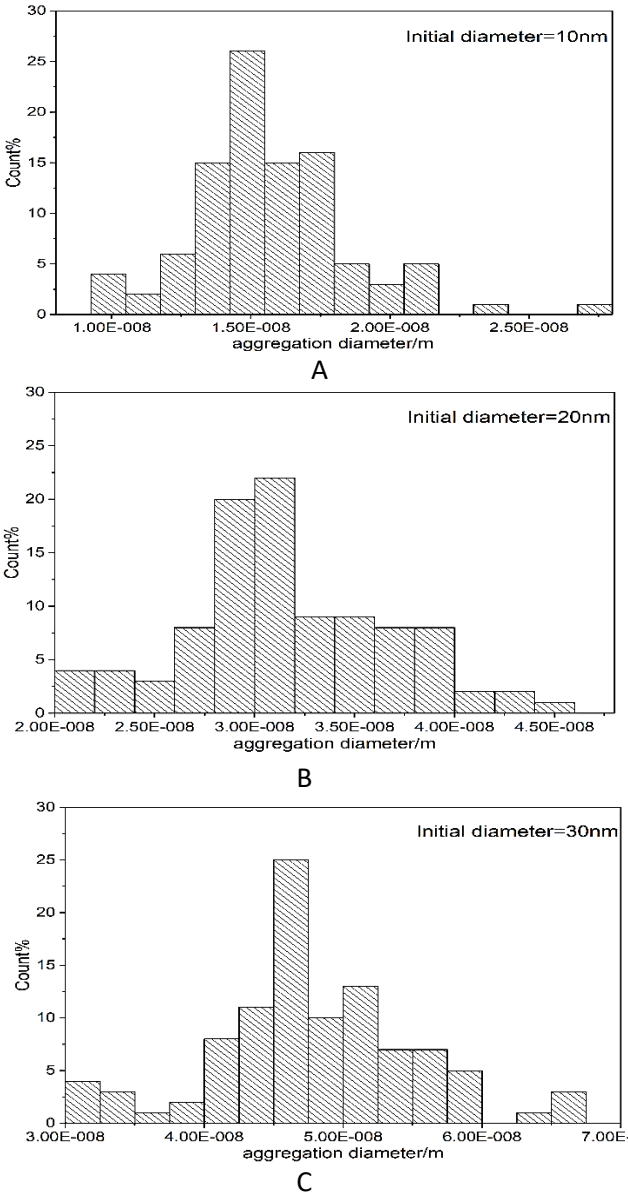

Fig.3. Diameter distribution of different size nanoparticle (N=3000)

The average increasements of particle size is shown in Fig 4. Each size is simulated 5 times and take the average diameter of all nanoparticles in the simulation box.

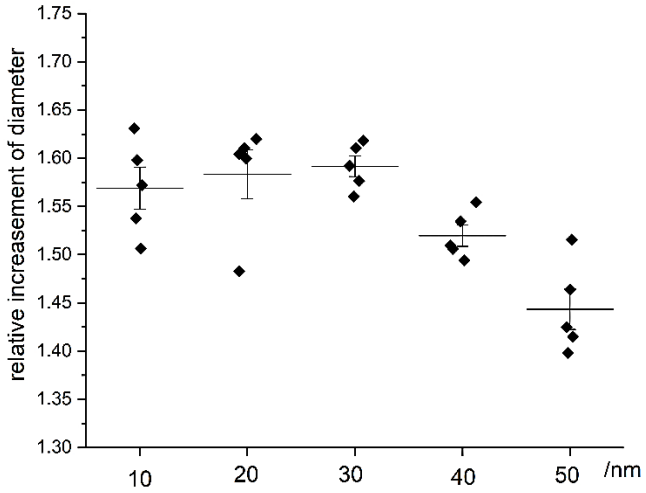

Fig.4. Relative increasement of particle with different size

According to DLVO theory, energy barrier decreases when the size of particle is reducing, likewise, small size contributes to more intense Brownian motion, thus the attachment efficiency will be higher for particles with small size. In Fig.3. the relative average aggregation size has an obvious decrease over the range of 30-50 nm, this

result indicates the larger size may lead to more stable colloidal system and kinetic Monte Carlo is able to predict the aggregation phenomenon of colloidal system. Further, the effect of pH, mass fraction and temperature will be studied and the experiments will be designed for checking the simulation results.

ACKNOWLEDGEMENT

This work was supported by the funding of Nature Science Foundation of China (U1707603).

REFERENCE

[1] Ruijin Wang, Sheng Qian, Zhiqi Zhang. Investigation of the aggregation morphology of nanoparticle on the thermal conductivity of nanofluid by molecular dynamics simulations[J]. International Journal of Heat and Mass Transfer, 2018, 127:1138-1146.

[2] Vaibhav Somani. Colloidal stability of magnetic nanoparticles in molten salts[D]. MASSACHUSETTS INSTITUTE OF TECHNOLOGY, 2010.

[3] Liu H H , Surawanvijit S , Rallo R , et al. Analysis of Nanoparticle Agglomeration in Aqueous Suspensions via Constant-Number Monte Carlo Simulation[J]. Environmental Science & Technology,2011, 45(21):9284-9292.

[4] Song Y , Bhadeshia H , Suh D . Stability of stainless-steel nanoparticle and water mixtures[J]. Powder Technology, 2015, 272:34-44.

[5] Zhang W. Nanoparticle Aggregation: Principles and Modeling[J]. Advances in Experimental Medicine & Biology, 2014, 811:19.

[6] Smith M , Matsoukas T . Constant-number Monte Carlo simulation of population balances[J]. Chemical Engineering Science, 1998, 53(9):1777-1786.

[7] Lingnan Lin, Hao Peng, Guoliang Ding. Model for predicting particle size evolution during nanoparticle aggregation in refrigerant–oil mixture[J]. International Journal of Heat and Mass Transfer, 2018, 119:91-104.

[8] Bonitz M , Becker K , Lopez J , et al. Complex Plasmas: Scientific Challenges and Technological Opportunities[J]. Apress, 2014.