OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 9, No. 3-4, March – April 2015, p. 497 - 501

A modified prediction model for viscosity of nanofluids based on molecular dynamics simulation

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Classical viscosity predicting models for conventional-scale particle suspensions failed to predict viscosities of nanofluids. Based on molecular dynamics simulation, the present work deliberated on the effects of absorption layer and nanoparticle agglomeration, and presented a modified predicting model for viscosity of nanofluids. The predicting values of the modified model for viscosities of nanofluids were well in agreement with experimental results. The diameter of nanoparticle agglomeration and thickness of absorption layer were found to be important influencing factors for viscosities of nanofluids that should be considered.

(Received January 22, 2015; accepted March 19, 2015)

Keywords: Nanofluids, viscosity predicting model, Absorption layer, Nanoparticle agglomeration

1. Introduction

The concept of nanofluids refers to the new type of heat transfer medium which is prepared by dispersing metallic or non-metallic nanoparticles into traditional heat transfer fluids such as water, oil, or alcohol [1]. Extensive concerns have been given to nanofluids for the numerous advantages that they possess including the significant increased thermal conductivity, good suspension stability, and low pressure drop caused, which makes them develop rapidly [2-5]. Due to the small scale effect of nanoparticles [6-8], nanofluids exhibit various unique properties that cannot be explained by classic theories. Before nanofluids could be used in industrial production applications, a comprehensive and systematic understanding on the characteristics of these new fluids should be obtained.

As a heat transfer fluid, the measuring of viscosity and constructing of viscosity predicting model are essential for nanofluids. Scholars have conducted extensive experimental measurements, among which material of nanoparticles mainly concerns Al_2O_3 [2-4,6,10], SiO_2 [11,12], TiO_2 [13-18], CuO [10,19,20]; base fluids includes water, ethylene glycol(EG) [17-19], propylene glycol(PG) [4], and ethanol(Eth) [12]; diameter scope of nanoparticles is 25nm-200nm; volume concentration range of nanoparticles is 0.01%-7.1%; and testing temperature range is 293K-333K. According to literatures reported, there is slight increase in the viscosity of nanofluids compared to those of base fluids, and the variation law of viscosity differs from that of conventional large scale particles suspensions. Therefore various influencing factors for viscosities of nanofluids have been discussed, mainly concerns volume concentration, PH value, dispersants, nanoparticle agglomeration and spatial distribution patterns, Brownian motions of nanoparticles, and the absorption layer of liquid molecules on the surface of nanoparticles [20-28].

For viscosity of nanofluids, the predicted value by conventional viscosity predicting model for conventional-scale particle suspensions is significantly lower than that of experiments [13, 19, 20], therefore the predicting model needs to be modified. Yet a fitting formula according to experiment results is merely suitable for certain conditions and with lack of physical significance. The present work deliberated on effects of the absorption layer and nanoparticle agglomeration, and presented a modified predicting model for viscosity of nanofluids.

2. Predicting model for viscosity of nanofluids

2.1 Classical viscosity predicting models

So far, there are a host of semiempirical formulas for viscosities of binary fluids containing conventional-scale solid particles. Most of them are on the basis of the following formula:

$$\mu = \mu_f \frac{(1+0.5\varphi)}{(1-\varphi)^2} \tag{1}$$

The equation above is the noted Einstein equation for the viscosity of binary fluids [29], in which μ is viscosity of the mixture, μ_f is viscosity of base liquid, and φ is volume concentration of particles. Without considering interactions between particles when the volume concentration is low (φ<0.05), the equation could be simplified as:

$$\mu = \mu_f (1+2.5\varphi) \tag{2}$$

With consideration of interactions between particles, Batchelor modified Einstein equation as [30]:

$$\mu = \mu_f (1+2.5\varphi+6.25\varphi^2) \tag{3}$$

Zuzovsky further refined Einstein equation as [31]:

$$\mu/\mu_f = 1+\frac{2.5\varphi}{1+0.0862\varphi-2.286\varphi^{5/3}} \tag{4}$$

According to the study of De Kruif *et al.* [32], two-order approximation method is the only difference between these equations. In fact, predicting results of these equations are almost the same. But when it comes to nanofluids, all predicting values of these equations are with large errors compared to the results of experiment [20]. It is partly because of these models are based on the following hypothesis: Interactions between suspended particles are ignored, the suspension is in the laminar flow, and viscosity of suspension is the contribution of all suspended particles for the entire field of shear force. Therefore, aiming at nanoparticles suspensions, the viscosity predicting model should be modified.

2.2 Nanoparticle agglomeration described by fractal theory

Under the combined action of Brownian motion force and van der Waals force, in the process of random motion, the suspended nanoparticles in nanofluids would collide and agglomerate with each other, and nanoparticles would form into nanoclusters. During the subsequent random motion, the nanoparticle group would agglomerate with other nanoparticle or nanoparticle group to form larger nanoclusters. Results of numerical simulation and experiments show that, the characteristics of nanoclusters in nanofluids are complex structure and coexistence of big and small nanoparticle group [33]. Besides, the nanocluster massed by nanoparticles is not compact in structure but presents bifurcation. According to the study of Wang et al. [20], fractal theory could be used to well describe the random agglomeration and differentiation process of nanoparticles in mesoscopic state [34]. The volume concentration of nanoparticles in an agglomeration is defined as:

$$\varphi_{np,cl} = \left(\frac{d_{cl}}{d_{np}}\right)^{D-3} \tag{5}$$

where d_{cl} is diameter of nanoparticle agglomeration, d_{np} is the diameter of single spherical nanoparticle, D is fractal dimension of the nanoparticle agglomeration.

2.3 Determination of the thickness of absorption layer

The experimental results of Yu *et al.* [35] and the molecular dynamics simulations performed by Xue *et al.* [36] showed that liquid molecules close to nanoparticles would be absorbed to solid surface and the typical interfacial layer thickness between the solid and liquid phases is of the order of a few atomic distances. The absorption layer on surface of nanoparticles would significantly increase the effective dimension which makes the effective volume friction of nanoparticles increase.

Based on the electron density profile at the interface, Hashimoto *et al.* [37] established a definition of the absorption layer thickness at the surface of spherical micro-domains, which is given as

$$t = \sqrt{2\pi}\sigma \tag{6}$$

Which σ is a parameter characterizing the diffuseness of the interfacial boundary. Its typical value falls in the range of 0.3-0.6nm. Thus the thickness of absorption layer is in the range of 0.75-1.5nm.

In order to determine the thickness of absorption layer, the present work has performed molecular dynamics simulations on Cu-Ar nanofluids with different nanoparticle diameters. The simulation models are set to be cubic consisting of one Copper nanoparticle with diameters of 1nm and 4nm in the center and Argon atoms around making both the volume concentrations are 1%. Different diameter of nanoparticle is to examine the effect of naoparticle size for the thickness of absorption layer. The thickness of absorption layer is determined by statistical calculation of the density distribution of the argon form the center of the nanoparticle which is defined as [38]:

$$n = \frac{\Delta N}{\Delta V} \tag{7}$$

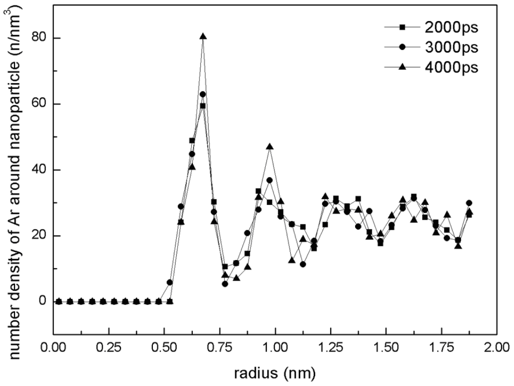
where ΔN is number of atoms within the volume ΔV. The computational domain around a nanoparticle is divided into many spherical shells and the numbers of atoms within each spherical shell are accounted to obtain the number density.

The amount of Copper atoms within the one nanometer particle is 43 and the total amount of atoms is 1360; for that of 4nm, it is 2850 and 72409, respectively. All atoms in simulation models are initially in Face-Center-Cubic (FCC) lattice. Lennard-Jones (LJ) potential function is used in the molecular dynamics simulation. The LJ parameters for argon are $\varepsilon_{Ar}=1.67\times10^{-21}$ J and $\sigma_{Ar}=0.3405$ nm [39]. For copper, the LJ parameters are $\varepsilon_{Cu}=65.625\times10^{-21}$ J and $\sigma_{Cu}=0.2338$ nm [39].

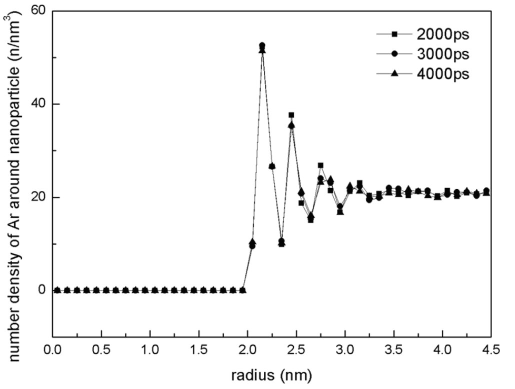
According to Lorentz-Berthlot mixing law [40], ε and σ between copper and argon are 10.4153×10^{-21} J and 0.2872 nm, respectively.

The molecular dynamics simulation is performed on a 4 core parallel computer in NTV ensemble at constant temperature of 86K and the cut-off ratio is chosen to be $2.5\sigma_{Ar}$. Periodic boundary conditions are applied along all three directions. With each time step length of 2 fs, the initial simulation system is relaxed for 200 ps and running for 4000 ps. The results of latter are used for statistical calculation.

The simulation results of the density distribution of argon atoms around nanoparticles with diameters of 1nm and 4nm are shown in Fig. 1 and Fig. 2. Fig. 1 shows the statistical calculated number density of Ar atoms around nanoparticle at simulation time of 2000, 3000, and 4000 ps. It could be found that along the radial direction there exist four peak values of number density by which the thickness of absorption layer could be estimated. In Fig. 2 we have presented a more intuitive picture for the thickness of absorption layer with different diameters of nanoparticle. It could be found that with a smaller diameter, the thickness of absorption layer has not signally changed, but the number of Ar atoms being absorbed is slightly increased. In this situation, the thickness of absorption layer is approximately 1.25nm. When the base fluid is water or other materials, the value should be revised.



(a) Diameter of nanoparticle is 1 nm



(b) Diameter of nanoparticle is 4 nm

Fig. 1. Number density of Ar around nanoparticle at different simulation time.

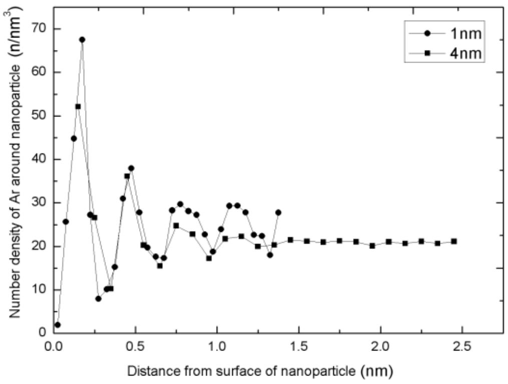


Fig. 2. Comparison of thickness of absorption layer with different diameters.

In fact, according to the studies of Wang et al. [20], the absorption behaviour in nanoparticles suspension of low concentration belongs to monolayer adsorption, and the thickness of absorption layer could be estimated by Langmuir monolayer adsorption equation:

$$d_{ab} = \frac{1}{\sqrt{3}}\left(\frac{4M}{\rho_f N_A}\right)^{1/3} \tag{8}$$

where M, ρ_f, and N_A are molecule weight, density of fluid, and Avogadro constant.

With consideration of the absorption layer, the volume concentration of nanoparticles in nanofluids is:

$$\varphi'_{np,nf} = \varphi_{np,nf}\left(1+2\frac{d_{ab}}{d_{np}}\right)^3 \tag{9}$$

2.4 Modified predicting model for viscosity of nanofluids

According to principle of mass conservation, volume concentration of the spherical nanoparticle agglomeration in fluids is defined as [41]:

$$\varphi_{cl,nf} = \varphi'_{np,nf} \big/ \varphi_{np,cl} \tag{10}$$

On the basis of Einstein equation, considering effects of nanoparticle agglomeration and absorption layer, the predicting model for viscosity of nanofluids could be written as:

$$\mu = \mu_f\left(1+2.5\varphi_{np,nf}\,\frac{\left(1+2\dfrac{d_{ab}}{d_{np}}\right)^3}{\left(\dfrac{d_{cl}}{d_{np}}\right)^{D-3}}\right) \tag{11}$$

According to the study of Jiang *et al.* the value of D could be set to 2.64 [42]. The value of d_{cl} is decided by preparing conditions of nanofluids as physical or chemical treatment would restrain agglomeration of nanoparticles in nanofluids. Based on the study of Hong et al., generally the value of d_{cl} could be set in the range of 0.5-2.5μm [43].

3. Results and discussion

The modified model is applied to predict viscosities of CuO-H_2O nanofluids with different volume concentrations and compared to the results of experiments [20]. With the average diameter of nanoparticle of 50nm, the value of d_{cl} is set as 0.5μm, and d_{ab} is 2.8nm as Wang et al. calculated. The predicting values are very close to experimental results with the maximum error of 2.52%, as shown in Fig. 3. Fig. 4 shows the comparison between prediction and experimental results for viscosity of Al_2O_3-H_2O with the present model [44]. It could be found that the predictions is quite close to experimental results, and the maximum error is 2.6% when the nanoparticle volume concentration is 2%. The present model is applied to predict the viscosity of SiO_2-H_2O nanofluids at different temperatures, as shown in Fig. 5. It could be found that the present model can successfully predict the influence of temperature for nanofluids. In the predictions the average diameter of nanoparticles is set to be 40nm and 20nm; the diameter of cluster is 179nm and 150nm respectively; the fractal dimension is chosen to be 2.4 and 2 respectively [45]; the thickness of absorption layer is 1nm.

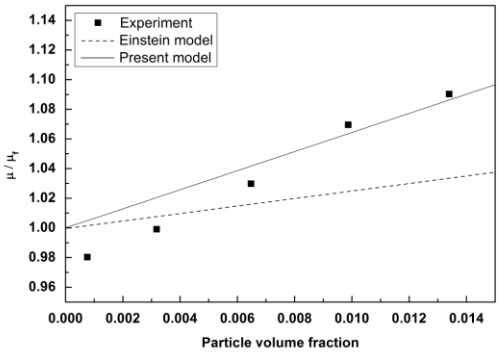


Fig. 3. Comparison of viscosity of CuO-H_2O nanofluid between prediction and experiment.

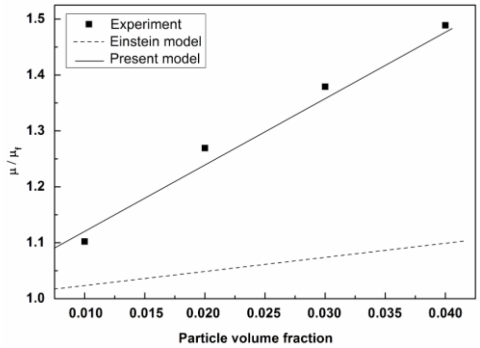


Fig. 4. Comparison of viscosity of Al_2O_3-H_2O nanofluid between prediction and experiment.

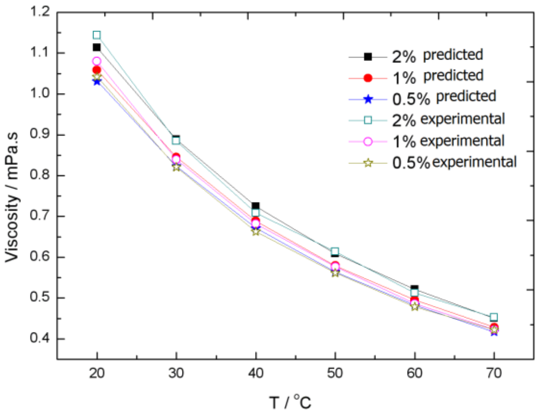


Fig. 5. Prediction of the present model for viscosity of SiO_2-H_2O nanofluids at different temperatures.

Through analysis of the modified model, besides average diameter and volume concentration of nanoparticles, both the diameter of nanoparticle agglomeration d_{cl} and thickness of absorption layer d_{ab} are influencing factors for viscosities of nanofluids. With sufficient physical or chemical treatment, the diameter of nanoparticles agglomeration would be effectively reduced and the viscosities of nanofluids would not be significantly increased according to equation (11). The molecular dynamics simulation results show that the thickness of absorption layer is not related to the diameter of nanoparticle but mainly concerned with attributes of base fluid. With a decreasing nanoparticle size, the amount of liquid molecules being absorbed within the absorption layer is increasing.

4. Conclusions

Based on the classic Einstein equation for viscosity of binary fluids, the present work has considered effects of agglomeration of nanoparticles and absorption layer of liquid molecules to modify the viscosity predicting model. Fractal theory has been used to describe the phenomenon of nanoparticle agglomeration in nanofluids. In order to determine the effect of absorption layer, a molecular dynamics simulation has been performed to examine the relationship between thickness of absorption layer and diameter of nanoparticle. The predicting values of the modified model for viscosities of various types of nanofluids are well in agreement with experimental results. The diameter of nanoparticle agglomeration and thickness of absorption layer are important influencing factors for viscosities of nanofluids that should be considered.

Acknowledgments

China Postdoctoral Science Foundation funded project

(Grant No. 2014T70330, 2013M540284). Project (HIT.NSRIF.2015116) supported by Natural Scientific Research Innovation Foundation in Harbin Institute of Technology. Project (HIT(WH)201301, HIT(WH)201406) supported by Scientific Research Foundation of Harbin Institute of Technology at Weihai. We acknowledge the reviewers' comments and suggestions very much, which are valuable in improving the quality of our manuscript.

References

[1] S. U. S. Choi, Developments and Applications of Non-newtonian Flows New York, USA, 99 (1995).
[2] S. K. Das, N. Putra, W. Roetzel, Int. J. Heat. Mass. Trans. **46**, 851 (2003).
[3] N. Putra, W. Roetzel, S. K. Das, Heat. Mass. Trans. **39**, 775 (2003).
[4] R. Prasher, D. Song, J. Wang, P. Phelan, Appl. Phys. Lett. **89**, 133108 (2006).
[5] X. F. Zhou, L. Gao, Chinese Physics B **16**, 2028 (2007).
[6] X. Wang, X. Xu, S. U. S. Choi, J. Thermophys. Heat Trans. **13**, 474 (1999).
[7] H. Ding, C. M. Shen, C. Hui, Z. C. Xu, C. Li, Y. Tian, X. Z. Shi, H. J. Gao, Chinese Physics B **19**, 066102 (2010).
[8] L. Wang, F. S. Li, Chinese Physics B **17**, 1858 (2008).
[9] J. H. Lee, K. S. Hwang, S. P. Jang, B. H. Lee, J. H. Kim, S. U. S. Choi, C. J. Choi, Int. J. Heat. Mass. Trans. **51**, 2651 (2008).
[10] X. F. Peng, Study of Nanofluids Heat Transfer Performance in High Temperature Condition Based on Vehicular Cooler (Ph.D. Thesis) (Hangzhou: Zhejiang University) (in Chinese) (2007).
[11] S. S. Guo, Z. Y. Luo, T. Wang, J. F. Zhao, K. F. Cen, Bulletin of the Chinese Ceramic Society **25** 52 (in Chinese) (2006).
[12] J. Chevalier, O. Tillement, F. Ayela, Appl. Phys. Lett. **91**, 233103 (2007).
[13] H. Masuda, A. Ebata, K. Teramae, N. Hishinuma, Netsu Bussei **4**, 227 (1993).
[14] B. C. Pak, Y. I. Cho, Exp. Heat. Trans. **11**, 151 (1998).
[15] Y. He, Y. Jin, H. Chen, Y. Ding, D. Cang, H. Lu, Int. J. Heat. Mass. Trans. **50**, 2272 (2007).
[16] Y. D. Liu, K. N. Li, M. W. Tong, Q. B. He, B. Liu, S. L. Chen, Journal of Chongqing University (Natural Science Edition) **29**, 52 (2006) (in Chinese).
[17] H. Chen, Y. Ding, C. Tan, New J. Phys. **9**, 367 (2007).
[18] H. Chen, Y. Ding, Y. He, C. Tan, Chem. Phys. Lett. **444**, 333 (2007).
[19] J. Garg, B. Poudel, M. Chiesa, J. B. Gordon, J. J. Ma, J. B. Wang, Z. F. Ren, Y. T. Kang, H. Ohtani, J. Nanda, G. H. McKinley, G. Chen, J. Appl. Phys. **103**, 074301 (2008).
[20] B. X. Wang, L. P. Zhou, X. F. Peng, Prog. Nat. Sci. **14**, 799 (2004) (in Chinese).
[21] S. Ramakrishnan, C. F. Zukoski, J. Chem. Phys. **113**, 1237 (2000).
[22] A. A. Zaman, P. Singh, B. M. Moudgil, J. Colloid Interface Sci. **251**, 381 (2002).
[23] W. J. Tseng, C. H. Wu, Acta Mater. **50**, 3757 (2002).
[24] W. J. Tseng, K. C. Lin, Mater. Sci. Eng. A **355**, 186 (2003).
[25] J. M. Li, Z. L. Li, B. X. Wang, Tsinghua. Sci. Tech. **7**, 198 (2002).
[26] M. Corcione, Energy Convers. Manage. **52**, 789 (2011).
[27] M. S. Hosseini, A. Mohebbi, S. Ghader, Chin. J. Chem. Eng. **18**, 102 (2010).
[28] D. P. Kulkarni, D. K. Das, G. A. Chukwu, J. Nanosci. Nanotechno. **6** 1150 (2006).
[29] A. Einstein, Investigations on the theory of the Brownian movement (New York: Dover) 9-15 (1956).
[30] G. K. Batchelor, J. Fluid Mech. **83**, 97 (1977).
[31] M. Zuzovsky, P. M. Adler, H. Brenner, Phys. Fluids **26**, 1714 (1983).
[32] C. G. De Kruif, E. M. F. Van Lersel, A. Vrij, W. B. Russel, J. Chem. Phys. **83**, 4717 (1985).
[33] Y. M. Xuan, Q. Li, Theory and Application of Energy Transfer in Nanofluids (Beijing: Science Press) 33 (in Chinese) (2010).
[34] B. B. Mandelbrot, The Fractal Geometry of Nature (San Francisco: W H Freeman Publisher) 63 (1982).
[35] C. J. Yu, A. G. Richter, A. Datta, M. K. Durbin, P. Dutta, Physica B **283**, 27 (2000).
[36] L. Xue, P. Keblinski, S. R. Phillpot, S. U. S. Choi, J. A. Eastman, Int. J. Heat Mass Tran. **47**, 4277 (2004).
[37] T. Hashimoto, M. Fujimura, H. Kawai, Macromolecules **13**, 1660 (1980).
[38] L. Li, Y. W. Zhang, H. B. Ma, M. Yang, Phys. Lett. A **37**, 4541 (2008).
[39] S. Sarkar, R. P. Selvam, J. Appl. Phys. **102**, 074302 (2007).
[40] M. P. Allen, D. J. Tildesley, Computer Simulation of Liquids (Oxford: Clarendon Press) 21 (1987).
[41] G. L. Ding, W. T. Jiang, H. Peng, H. T. Hu, J. Eng. Thermophys. **31**, 1281 (2010) (in Chinese).
[42] W. T. Jiang, G. L. Ding, H. Peng, Y. F. Gao, K. J. Wang, HVAC&R Research **15**, 651 (2009).
[43] K. S. Hong, T. K. Hong, H. S. Yang, Appl. Phys. Lett. **88**, 031901-1-031901-3 (2006).
[44] P. Florova, P. Sklenovsky, P. Banas, M. Otyepka, J. Chem. Theory Comput. **6**, 3569 (2010).
[45] S. Izvekov, G. A. Voth, J. Chem. Phys. **123**, 134105 (2005).

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