Modified Maxwell model for predicting thermal conductivity of nanocomposites considering aggregation*

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The effect of nanoparticle aggregation on the thermal conductivity of nanocomposites or nanofluids is typically non-negligible. A universal model (Maxwell model) including nanoparticle aggregation is modified in order to predict the thermal conductivity of nanocomposites more accurately. The predicted thermal conductivities of silica and titania nanoparticle powders are compared first with that measured by a hot-wire method and then with those in previous experimental works. The results show that there is good agreement between our model and experiments, and that nanoparticle aggregation in a nanocomposite enhances the thermal conductivity greatly and should not be ignored. Because it considers the effect of aggregation, our model is expected to yield precise predictions of the thermal conductivity of composites.

Keywords: thermal conductivity, nanocomposite, aggregation, titania

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1. Introduction

Nanocomposites have attracted considerable attention for their potential applications as thermoelectric[1–4] and thermal insulation materials.[5–9] Thermal conductivity is one of the most important properties of nanocomposites because of its strong effect on the thermoelectric or thermal insulation properties.[10–13] Some models have been developed to predict the thermal conductivity of composites. The earliest thermal conductivity model for composites was established by Maxwell and Rayleigh,[14] and further models have been established for nanocomposites, details of which can be found in Refs. [15]–[25]. Because aggregation of nanoparticles is difficult to avoid, and previous models are too complicated or were established without considering aggregation, a Maxwell model based on a two-level structure model and considering nanoparticle aggregation is modified to accurately predict the thermal conductivity of nanocomposites in this paper. A comparison with the experimental thermal conductivities of silica and titania nanoparticle powders, which are special nanocomposites with nanoparticles embedded in an air matrix, reveals that the thermal conductivity predicted by our model agrees well with that obtained experimentally. Furthermore, agreement between our model and earlier experimental works is also observed. In the following, we first introduce the experimental method. The modified Maxwell model is then deduced. Finally, the model and the experimental results are compared and discussed.

2. Hot-wire method and material characterization

The hot-wire method, which is a type of transient method widely used in scientific research,[26–29] is applied in this paper to measure the thermal conductivity of nanoparticle powders. In this method, the hot wire, which acts as an electrical heating source, is embedded in the sample material, and a thermocouple is placed at a distance from the hot wire. When a fixed heating flow is loaded on the wire, the thermal conductivity can be calculated from the temperate gradient over a given time interval. When the thermocouple is located on the wire, the thermal conductivity is calculated as[6]

$$k = \frac{q}{4\pi}\frac{\ln t_2 - \ln t_1}{T_2 - T_1}, \tag{1}$$

where q is the electric heating power per unit length, and T_2 and T_1 are the temperatures at times t_2 and t_1, respectively.

A schematic diagram of the hot-wire system is shown in Fig. 1. A data acquisition instrument (TC3000, Xi'an Xiatech Electronic Technology Co. Ltd., China) is applied to record the temperature with increasing time, and a 76.2-μm-diameter platinum wire acts as both a heater and resistance thermometer, as shown in Fig. 1(b). The platinum wire is coated with a thin layer of epoxy resin to prevent oxidation. In the measurement, the hot wire is embedded in the nanoparticle powder. The porosity of the nanoparticle powder depends on the pressure loaded on it. After the temperature–time curve is obtained, the thermal conductivity of the sample can be easily calculated with an instrumental error of less than 3%. Every sample is measured six times, and the mean thermal conduc-

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tivity is obtained. The porosity of a sample is calculated as $\varphi = 1 - \rho_1/\rho_2$, where ρ_1 is the density of the sample, and ρ_2 is the density of the corresponding bulk material. The density of the sample is calculated as $\rho_1 = m/V$, where m is the mass of the sample measured by an electronic balance with an uncertainty of 0.0001g, and V is the volume of the sample calculated as the cross-sectional area multiplied by the thickness. Here the cross-sectional diameter and thickness are measured by a spiral micrometer with an uncertainty of 0.001 mm. The ρ_2 values of bulk silica and titania are 2.2×10^3 and 3.9×10^3 kg/m^3, respectively. The porosity uncertainty is calculated to be less than 0.0001, which is small enough to ignore.

Titania nanoparticle powders (TNPs) with diameters of 5 and 50 nm and silica nanoparticles powders (SNPs) with diameters of 200 and 500 nm are used in the measurement. The temperature versus ln(t) plots of different samples are shown in Fig. 2. From Fig. 2, the thermal conductivity is calculated by Eq. (1). The porosity of the TNPs and SNPs is about 95% when no pressure is loaded. By applying a small pressure (less than 1 MPa), the porosity of the SNPs and TNPs can be reduced from about 95% to 90%. The nanostructures of the nanoparticle powders are observed with a scanning electron microscope (SEM, FEI Quanta TM 250), as shown in Fig. 3.

To represent the microstructure of the powders in Fig. 3, a two-level structure model is set up, as shown in Fig. 4. On the first level, the nanoparticle clusters are thought of as a composite consisting of nanoparticles and air. On the second level, the structure of the nanocomposites is divided into two parts, the nanoparticle clusters and air. On the basis of the structure model shown in Fig. 4, the Maxwell model will be modified to predict the thermal conductivity, as described in the next section.

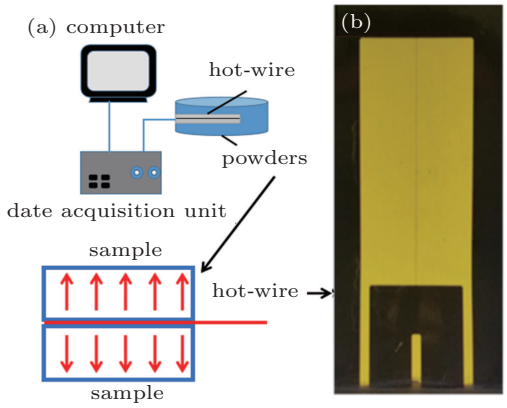


Fig. 1. (color online) Hot wire method: (a) schematic of the hot-wire system; (b) sensor.

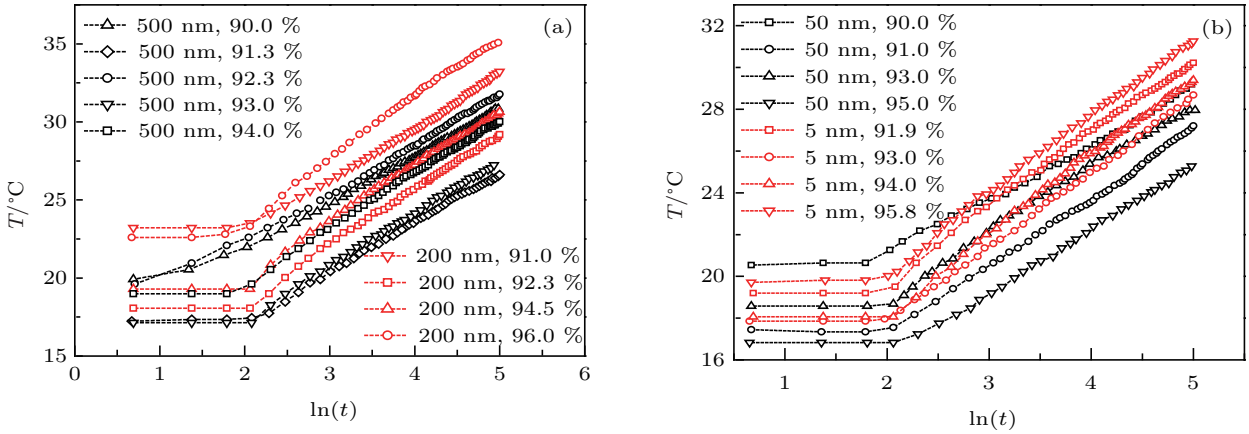


Fig. 2. (color online) Temperature versus ln(t), where t is the heating time in seconds: (a) 500- and 200-nm SiO_2 powders with different porosity; (b) 50 and 5 nm TiO_2 powders with different porosity.

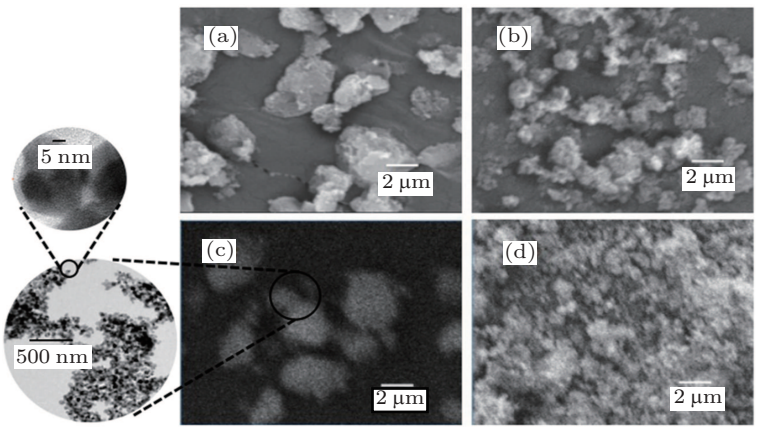


Fig. 3. (color online) Nanostructure of powders observed by SEM: (a) 500 nm and (b) 200 nm silica nanoparticles; (c) 50 nm and (d) 5 nm titania nanoparticles.

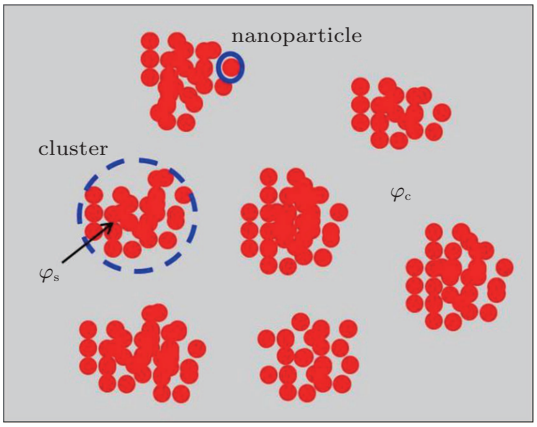


Fig. 4. (color online) Two-level structure model of nanocomposites.

3. Modified Maxwell model

As shown in Fig. 4, we define the volume fraction of nanoparticles in a cluster as φ_s and the volume fraction of clusters in the powder as φ_c. Thus, the overall porosity of nanocomposites is calculated as

$$\varphi = 1 - \varphi_s \varphi_c. \tag{2}$$

Because the diameters of the 200 and 500 nm silica nanoparticles and 50 nm titania nanoparticles are much larger than their bulk phonon mean free paths (40 nm for silica, 13 nm for titania), the size effect can be ignored.[30] Only the size effect of titania nanoparticles with a diameter of 5 nm should be considered. According to the phonon gas kinetic theory, the thermal conductivity of a nanoparticle can be approximately expressed as

$$k_s = \frac{1}{3} cvl, \tag{3}$$

where c is the specific heat capacity, v is the velocity of sound, and l is the phonon mean free path, which is estimated as follows:[31]

$$\frac{1}{l} = \frac{1}{l_0} + \frac{1}{R}. \tag{4}$$

Here R is the radius of the nanoparticles, and l_0 is the phonon mean free path of the bulk, which can be calculated as[32]

$$l_0 = \frac{20}{\varepsilon^2} \frac{T_m}{T} \alpha, \tag{5}$$

where ε is the Grüneisen constant ($\varepsilon = 2$ for titania), T_m is the melting temperature of the material (2123 K for titania), and α is the lattice constant (0.06635 nm for titania). The l_0 value calculated by Eq. (5) is 13 nm. When l_0 is substituted into Eq. (4), the phonon mean free path of titania particles with a 5-nm diameter is calculated to be 3.61 nm.

On the first level, the volume fraction of aggregated nanoparticles in a cluster is calculated as[24]

$$\varphi_s = \frac{D}{3} \left(\frac{R_a}{R} \right)^{D-3}, \tag{6}$$

where R is the diameter of the nanoparticles, $D = 2.64$ for nanoparticle clusters,[33] and R_a is the average diameter of the clusters estimated from the microstructure shown in Fig. 3, as listed in Table 1. When nanoparticles become aggregated, according to the parallel model, the thermal conductivity of the cluster can be expressed as

$$k_a = \varphi_s k_s + (1 - \varphi_s) k_g, \tag{7}$$

where k_g is the thermal conductivity of the air or matrix.

Table 1. Sizes of nanoparticles and clusters, and thermal conductivities of nanoparticles.

Material	R/nm	R_a/nm	k_s/W·m^{-1}·K^{-1}
silica	500	3600	1.38[34]
silica	200	1400	1.38
titania	50	1100	3.60
titania	5	120	1.00

On the second level, where the clusters are treated as a solid phase, we apply the Maxwell model to predict the effectivethermal conductivity:

$$k = k_g \left[\frac{k_a + 2k_g + 2\varphi_c (k_a - k_g)}{k_a + 2k_g - 2\varphi_c (k_a - k_g)} \right]. \tag{8}$$

The total porosity φ is obtained by a mass volume fraction method, and φ_s iscalculated by Eq. (6). When φ and φ_s are substituted into Eq. (2), φ_c can be calculated. By substituting φ_c and k_a, which is described by Eq. (7), into Eq. (8), the thermal conductivity of the two-level nanostructure can be expressed as

$$\begin{aligned} k = k_g \Bigg\{ & \frac{D}{3} \left(\frac{R_a}{R} \right)^{D-3} k_s + \left[3 - \frac{D}{3} \left(\frac{R_a}{R} \right)^{D-3} \right] k_g \\ & + 2 \frac{\varphi_n}{(D/3)(R_a/R)^{D-3}} \left[\frac{D}{3} \left(\frac{R_a}{R} \right)^{D-3} (k_s - k_g) \right] \Bigg\} \\ & \Bigg\{ \frac{D}{3} \left(\frac{R_a}{R} \right)^{D-3} k_s + \left[3 - \frac{D}{3} \left(\frac{R_a}{R} \right)^{D-3} \right] k_g \\ & - 2 \frac{\varphi_n}{(D/3)(R_a/R)^{D-3}} \left[\frac{D}{3} \left(\frac{R_a}{R} \right)^{D-3} (k_s - k_g) \right] \Bigg\}^{-1}. \end{aligned} \tag{9}$$

4. Results and discussion

Considering that some models for predicting the thermal conductivity of composites already exist, we first compare the experimental thermal conductivities with those predicted by a universal model (Maxwell model) without considering nanoparticle aggregation. The results are shown in Figs. 5(a) and 5(b). The thermal conductivity of the nanocomposites is much larger than that predicted by the Maxwell model for both SNPs and TNPs. Aggregation of nanoparticles is responsible

for the large experimental results, because it causes nanoparticles to adhere to each other and form a heat flow path. The large deviation of the Maxwell model from the experimental results suggests that models that do not consider aggregation are not suitable for predicting the thermal conductivity of nanocomposites. Thus, we modify the Maxwell model to provide a more accurate prediction of the thermal conductivity of nanocomposites. The thermal conductivities predicted by the modified Maxwell model are also compared with those obtained experimentally. The results are shown in Figs. 5(c) and 5(d). Considering that no fitting parameter is applied in the model, the agreement between the model and experiments for both SNPs and TNPs is adequate. The agreement also confirms that aggregation of nanoparticles could greatly enhance the thermal conductivity of nanocomposites.

In addition to our measurements, previous experimental results are also compared with those predicted by the modified Maxwell model. The results are presented in Fig. 6. The

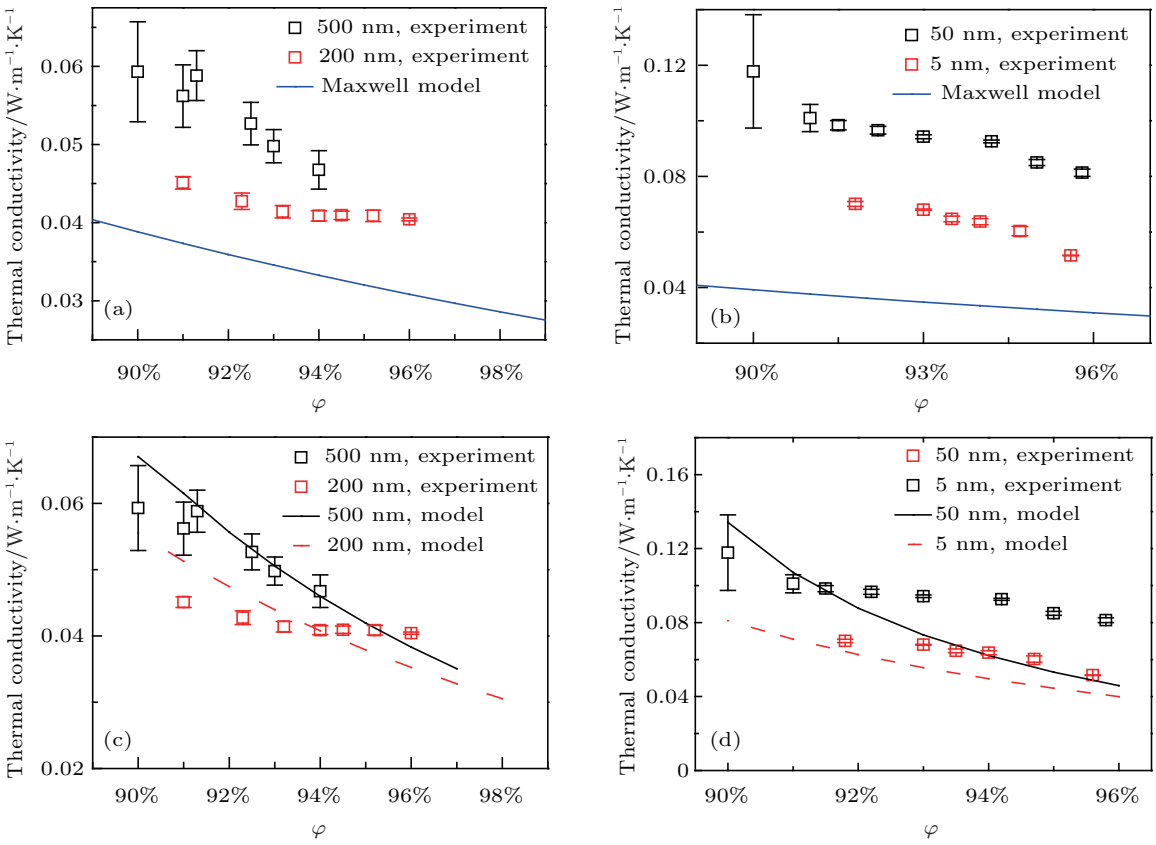


Fig. 5. (color online) Thermal conductivities of nanoparticle powders: (a) SNPs, Maxwell model and experiment. (b) TNPs, Maxwell model and experiment. (c) SNPs, modified Maxwell model and experiment. (d) TNPs, modified Maxwell model and experiment.

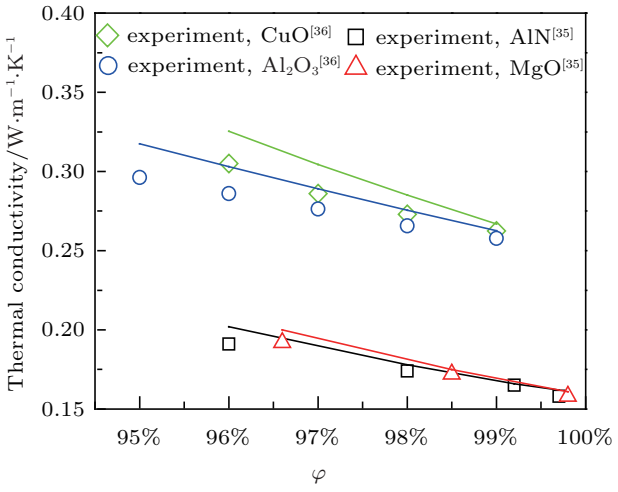


Fig. 6. (color online) Model validation.Lines represents the results predicted by the modified Maxwell model.

mean radii of clusters are estimated from the image of the microstructures shown in Refs. [35] and [36], as listed in Table 2. The thermal conductivities of the epoxy and ethylene glycol that are applied as the matrix in Refs. [34] and [35] are also listed in Table 2. Good agreement is found between the modified Maxwell model and the works of Machrafi *et al.*[35] and Lee and Choi.[36] The good agreement suggests wide applicability of the modified Maxwell model.

Table 2. Sizes of nanoparticles and clusters, and thermal conductivities of nanoparticles.[35,36]

Materials	R/nm	R_a/nm	k_s/W·m^{-1}·K^{-1}
AlN	54	230	2.70
MgO	53	150	3.32
Al_2O_3	19.2	70	30[37]
CuO	11.8	45	76.5[34]
Epoxy	–	–	1.91
Ethylene-glycol	–	–	0.25[34]

5. Conclusion

In this paper, considering nanoparticle aggregation, a Maxwell model based on a two-level structure model is modified to accurately predict the thermal conductivity of nanocomposites. In the model, the thermal conductivity of nanoparticles is calculated using a kinetic method. The volume fraction of clusters in the nanocomposites is derived from the relationship between the aggregation degree and the particle volume fraction. The thermal conductivities of SNPs and TNPs are measured by a hot-wire method, and the results are compared with that predicted by the modified Maxwell model. The thermal conductivity predicted by the modified Maxwell model agrees well with that obtained experimentally. Moreover, the agreement between our model and earlier experimental studies confirms the suitability of our model for predicting the thermal conductivity of nanocomposites. This modified Maxwell model can be used to predict the thermal conductivity of nanocomposites where aggregation should be not ignored, and to approximately estimate the thermal conductivity of nanoparticles if the thermal conductivity of the nanocomposites is known.

References

[1] Tang J, Wang H T, Lee D H, Fardy M, Huo H Z, Russell T P and Yang P 2010 *Nano Lett.* **10** 4279
[2] Lin Z Z, Huang C L and Huang Z 2017 *J. Nanosci. Nanotechnol.* **17** 1
[3] Dresselhaus M S, Chen G, Tang M Y, Yang R G, Lee H, Wang D Z, Ren Z F, Fleurial J P and Gogna P 2007 *Adv. Mater.* **19** 1043
[4] Lin Z Z, Huang C L, Zhen W K, Feng Y H, Zhang X X and Wang G 2017 *Nanoscale Res. Lett.* **12** 189
[5] Liu H, Li Z Y, Zhao X P and Tao W Q 2015 *J. Nanosci. Nanotechnol.* **15** 3218
[6] Huang C L, Lin Z Z, Feng Y H, Zhang X X and Wang G 2015 *Eur. Phys. J. Plus* **130** 239
[7] Li Z Y, Liu H, Zhao X P, and Tao W Q 2015 *J. Non-Cryst. Solids* **430** 43
[8] Feng D L, Feng Y H and Shi J 2016 *Acta Phys. Sin.* **65** 244401 (in Chinese)
[9] Liu H, Li Z Y, Zhao X P and Tao W Q 2016 *Int. J. Heat Mass Transfer* **95** 1026
[10] Zhang C B, Shen C Q and Chen Y P 2017 *Int. J. Heat Mass Transfer* **104** 1135
[11] Yu W and Xie H 2011 *J. Nanomater.* **2012** 435873
[12] Kulwinder K and Ranjan K 2016 *Chin. Phys. B* **25** 056401
[13] Yu W, Xie H, Yin L, Zhao J, Xia L and Chen L 2015 *Int. J. Therm. Sci.* **91** 76
[14] Rayleigh L 1976 *Philos. Mag.* **34** 481
[15] Prasher R S and Phelan P E 1999 *J. Heat Transfer* **123** 105
[16] Lotfizadeh S and Matsoukas T 2015 *J. Nanopart. Res.* **17** 1
[17] Eapen J, Rusconi R, Piazza R and Yip S 2010 *J. Heat Transfer* **132** 369
[18] Progelhof R C 1976 *Polym. Eng. Sci.* **16** 615
[19] Choi C J and Roberts N 2016 *Int. J. Therm. Sci.* **104** 13
[20] Siddiqui M U and Arif A F M 2016 *Materials* **9** 694
[21] Huang C L, Feng Y H, Zhang X X and Wang G 2014 *Eur. Phys. J. Appl. Phys.* **66** 67
[22] LotfizadehS and Desa T 2014 *APL Mater.* **2** 066102
[23] Huang C L, Qian X and Yang R G 2017 *EPL* **117** 24001
[24] Wang B X, Wang Zhou L P and Peng X F 2003 *Int. J. Heat Mass Transfer* **46** 2665
[25] Li X, Park W, Chen Y P and Ruan X L 2017 *J. Heat Transfer* **139** 022401
[26] Lin Z Z, Huang C L, Zhen W K and Huang Z 2017 *Appl. Therm. Eng.* **119** 425
[27] Huai X L, Tao Y J and Wang W W 2006 *Chin. Phys. Lett.* **23** 1511
[28] Xuan Y M and Li Q 2000 *Int. J. Heat Fluid Fl.* **21** 58
[29] Zhao D L, Qian X, Gu X K, Jajia S A and Yang R G 2016 *J. Electronic Packaging* **138** 040802
[30] Huang C L, Feng Y H, Zhang X X, Li J, Wang G and Chou A H 2013 *Acta Phys. Sin.* **63** 026501 (in Chinese)
[31] Ordonez-MirandaJ, Yang R G and Alvarado-GilJ J 2011 *Appl. Phys. Lett.* **98** 233111
[32] Dornhaus R, Nimtz P D G and Richter W 1976 *Solid-State Physics* (Germany: Springer Verlag)
[33] Jiang W T, Ding G L, Peng H, Gao Y F and Wang K J 2009 *HVAC&R Res.* **15** 651
[34] Hwng Y J and Ahn Y C 2006 *Curr. Appl. Phys.* **6** 1068
[35] Machrafi H, Lebon G and Iorio C S 2016 *Compos Sci. Technol.* **130** 78
[36] Lee S and Choi S 1999 *J. Heat Trans.-T ASME* **121** 280
[37] Sim L C and Ramanan S R 2005 *Thermochim. Acta* **430** 155