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Thermal conductance of randomly oriented composites of thin layers

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Abstract

This work studied the thermal conductance of thin layers with randomly oriented composites by the percolation theory, and developed an effective-medium approximation (EMA) model for triple bond percolation systems. The results showed that the thin layer is anisotropic in conductivities when its thickness is lower than the correlation length. The conductivity in normal direction increases with decreasing thickness while the in-plane conductivity declines. The significance of this thickness effect is a function of the concentration of good conductor and the thermal conductivity ratio of the phases in the composites. A threshold concentration exists for the conductivity of bulk composites, beyond which the effective thermal conductivity increases significantly from that of the poor conductor with increasing concentration.

The developed EMA model agrees quite well with the numerical simulation and is expected being applicable to predict thermal conductivities of composites using the coordination number as a fitting parameter

Keywords: Randomly oriented composites; Thin layers; Anisotropic; Conductivity; Percolation; Effective-medium approximation

1. Introduction

Composite materials are applied extensively in industries. For example, gas–solid composites for thermal insulation, conductive adhesive pastes, mixture of liquid/solid materials and metal powders, sorption agents for absorb-refrigeration and phase-change heat reservoir, are all composite materials. The thermal conductance of these materials is one of the topics of interest both for application purposes and for fundamental understanding.

The study of thermal characteristics of the bulk composite materials has been developed. It is often assumed that the composites are composed of representative periodical unit cells [1–4]. The conductive characteristics of the unit represent the bulk property of the composite material. One can obtain these characteristics of the composite material by studying the effective-conductivity of the unit cell. The hypothesis of periodical unit cell extremely simplifies the composite structure and makes the solution of heat conduction relatively easy. For a bulk composite material, each unit is very small compared with the bulk size and the material is macroscopically uniform.

However, composites are often applied between two

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Nomenclature

k	thermal conductivity
$k\perp$	the conductivities in normal directions
$k\vert$	the conductivities in-plane directions
k_1	the conductivity of good conductor
k_2	the conductivity of poor conductor
k_a	thermal conductivity of the bond in which one neighboring cell is good conductor and another is poor conductor
m	layer thick in x direction
p	probability or concentration of the good conductor cell
p_c	threshold concentration
$p_{c,2}$	threshold concentration in 2D system
$p_{c,3}$	threshold concentration in 3D system
Q	heat-conduction quantity
S	the conduction area
t	index
t_2	index for 2D system
t_3	index for 3D system
z	average coordination number
ΔT	the temperature difference
Δx	the conduction distance
ν_3	universal index
ε	three-dimensional percolation correlation length

solid surfaces, such as the conducting paste. When the composites are very thin or the percentage of the good conductor is low, the composites could not be recognized as uniform, and hence, a unit cell could not represent the properties of the composites anymore. The effects of random arrangement of unit cells should have to be considered. In this paper, ‘thickness’ or layer number refers to the relative thickness that is the ratio of the thickness over the typical size of the particles in the composites.

The studies of transport phenomena related to disordered features of composites started relatively late. Kirpatrick [5] in 1971 put forward the effective-medium approximation theory (EMA) to predict the electrical conductivity of disordered composite materials. Zhang and Stroud [6] applied EMA to the resistance model to investigate the in-plane electrical conductivity of thin layers composed of conducting and non-conducting materials, and found that the effective resistance had a transition from two-dimension to three-dimension with the increase in layer thickness. The EMA model agrees quite excellently with the computer experiments of the in-plane electrical conductivities of the thin layer composites with bond percolation. Neimark [7] derived the relation of electrical conductivity with the concentration of good conductor and the layer number for randomly oriented composites by fractal and percolation theory. The variation of critical concentration (at which percolation occurs for the first time) of good conductor with layer numbers in the in-plane direction was also derived. The predicted critical concentration was found in consistent with EMA model [6]. The electrical conductivity model from [7] is relevant only close to percolation threshold (critical concentration) and is not suitable to analyze the data far from the critical concentration.

The studies of the anisotropic thermal conductance of thin layers of disordered composites are few. Phelan and Nimann [8] in 1997 applied the thermal resistance network and studied the thermal conductivity of two-dimensional thin layers of disordered composites by numerical scheme and statistical method. From the view of percolation, the conduction in a thin layer is not two-dimensional but three-dimensional and the dimension will affect the result. Liang et al. [9] applied percolation theory, simple effective-medium approximation (EMA) and probability statistics to investigate the thickness effect on the thermal conductivity of disorder composite layers, the research is more qualitative than quantitative.

Although no report of experimental research of the thickness effect on thermal conductivity for thin layers of disordered composites has been found, the thickness effect on electrical conductivity has already been experimentally observed [10,11]. Ottavi et al. [10] observed an increasing slope of resistance versus height for packed mixtures of conducting and non-conducting spheres, indicating an increase in the electrical conductivity with decreasing thickness.

Maaroof and Evans [11] measured the parallel resistance during the growth of Pt and Ni films. In the early stages of growth, small clusters nucleate on the substrate surface and grow into islands of the condensed phase. With continued deposition the islands grow until they come into contact, eventually creating a metallic network that in-fills then to form the continuous film. Maaroof and Evans [11] observed a decrease of the film resistance with increasing deposition thickness. The variations of the conductivity with thickness in such materials arise from the random distribution of clusters, not from the confinement of the mean free path of the heat carriers by boundaries. The conductivity of each component in the composites is assumed to be independent of the particle size. Recently, Michels et al. [12] applied thermal spray techniques to produce resistance-heating elements that provide very high heat fluxes to solid surfaces. They electrically insulated the surface to be heated by depositing an alumina layer on it, and on this layer, they deposited a thin metallic layer that served as an electrical heating element. The thickness of the insulating layer may in principle be determined by calculating the electrical resistance required to prevent significant current from conducting to the underlying copper layer to be heated, using the resistivity of sprayed alumina at an appropriate mean temperature. Their testing, however, showed that heaters deposited onto insulators having thickness in the predicted range (about 10 μm) had inadequate electrical insulation for air plasma spray films and high velocity oxygen fuel films. The reduction in the electrical insulation may also be caused from the thickness effect due to the disordered structure in the insulating layers.

Similar to the electrical conductivity, it is expected that there exists a thickness effect on thermal conductivity of thin layers of disordered composites. The present work discussed first the anisotropic thermal conductance for thin layers of randomly disordered composites from point of view of percolation and EMA model and derived an EMA model based on bond percolation. Then, computer experiments were applied to study quantitatively the thermal conductivities of thin layers of randomly disordered composites in the normal and in-plane directions. Finally, a comparison between analytical model and numerical result was made.

2. Thermal conductance of thin layers of randomly disordered composites

Fig. 1 shows a site percolation system to be analyzed. Each site is occupied either by one phase of good conductor cell (dark one) or by another phase of poor conductor cell (white one). The good and poor conductor cells are distributed randomly and they have constant thermal properties (that is, there is no size effect on each cell). The thermal conductivity of thin layers is the topic of interest in the present work. The number of layers in x direction is limited while the numbers of layer in other two directions are infinite. The variation of numbers of layers in x direction will affect the thermal conductivities both in the normal (x) and in-plane directions (y and z), which is called the layer effect.

2.1. The percolation model

The heat conduction in a two-phase disordered composite layer could be treated as a percolation process [9]. Fig. 1 shows a percolation layer, which is composed of m layer thick in x direction. Each cubic site is occupied either by a good conductor or by a poor conductor. The good conductor cells distribute in the whole layer randomly with a probability or concentration of p. A good conductor cell is either isolated by the adjacent poor conductor cells or connected to the adjacent good conductor cells to form a cluster, i.e., a set of connected good conductor cells bounded by poor conductor cells. When the probability of good conductor cells is low, the length of the cluster is short, and all clusters are finite ones. In other words, there is no path linking the top and bottom. The conductivity of the layer is close to that of poor conductor. When p is large, there is conductive path between top and bottom, or there are infinite clusters connecting the top and bottom. So the effective thermal conductivity of the composite is enhanced obviously. There is a threshold concentration p_c of good conductor cells statistically where for the first time the heat current can percolate from one edge to another through the cluster of good conductor. This cluster is called infinite one.

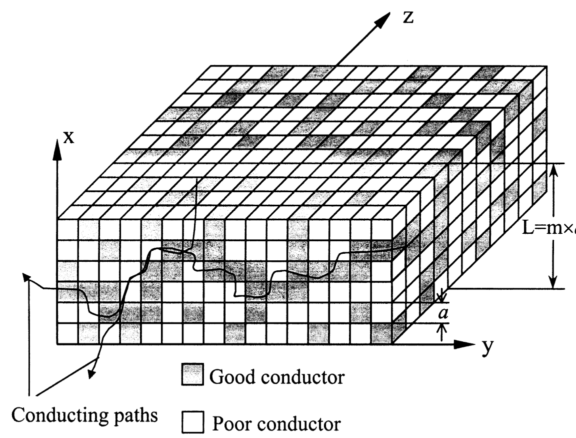

Fig. 1. A three-dimensional percolation layer composed of randomly disordered composite.

For a bulk composite material, the distribution of good and poor conductor could be regarded as uniform macroscopically although it may not be the case locally. For a thin layer, this local non-uniformity will give rise to changes in thermal conductivity from that of the bulk one in opposite trends in the normal and in-plane directions.

In the normal direction, with the increasing number of layers, the number of conducting paths joining the top and the bottom surface begin to reduce, which results in reduction in the heat-conduction quantity Q, and therefore, the effective thermal conductivity in normal direction declines. As an illustration, let's see a simple network of $2 \times 2 \times 1$ shown in Fig. 2. Suppose the good and poor conductor occupies half the sites in the network respectively. There will be two conducting paths of good conductor. If the thickness is doubled, the network becomes $2 \times 2 \times 2$. If there are two good conductor cells on the top and bottom respectively, the existence of two conductive paths of good conductor possess a probability of 25% and the probability of only one conductive path is 50%. The left 25% probability remains for the case where there is no conductive path of good conductor. Statistically, there is one conductive path. Actually, the conductive paths should be less than one if three to four good conductor cells exist in one layer. In this case the conduction area S and the temperature difference ΔT are constant, the distance Δx is doubled. According to the definition of thermal conductivity ($k = Q\Delta x / S\Delta T$), the thermal conductivity k is reduced because the heat flux Q becomes less than one half of its original value.

In the analysis of the in-plane conductivity, the length of conductive paths Δx and the temperature difference ΔT are invariable. As shown in Fig. 1 (for simplicity, it is assumed that identical number of infinite clusters appears in each layer), when the number of layer increase from one to two, finite clusters in each layer may join to form new infinite clusters. The total number of infinite clusters includes the ones in each layer and the ones formed between adjacent layers. Although the area S is doubled, the conductive paths are more than doubled, the effective thermal conductivity in the in-plane direction is increased. So there exists an anisotropic thermal conductance in thin layers of randomly distributed composites.

For the percolation system composed of $a \times a \times a$ cells shown in Fig. 1, it is more difficult to form an infinite cluster of good conductor connecting the top and bottom surface with increasing layer number. More percentage or concentration of good conductor cells would be required to form an infinite cluster. The threshold concentration depends on the thickness of the layer. For the percolation along y direction, when $m = 1$, the system is two-dimensional, and $p_c = p_c 2$ (where $p_{c,2}$ is the threshold concentration in 2D system); when $m \to \infty$, the system is 3D, and $p_c \to p_{c,3}$ (where $p_{c,3}$ is the threshold concentration in 3D system). The values of $p_{c,3}$ and $p_{c,2}$ depend on the lattice structure and types of percolation. For the problem of sites on a cubic lattice $p_{c,3} \approx 0.3117$–0.3333. For the problem of sites on a square lattice, $p_{c,2} \approx 0.5$–0.59275 [5–7,13]. For bond percolations, the thresholds are different. When the number of layer m equal to other value, p_c is between $p_{c,3}$ and $p_{c,2}$ [7]

$$p_c = p_{c,3} + (p_{c,2} - p_{c,3}) m^{-1/\upsilon_3} \tag{1}$$

where υ_3 is a universal index which describes the divergence of the three dimensional percolation correlation length $\varepsilon = a|p - p_c|^{-\upsilon_3}$. It is not difficult to understand this decrease of p_c with increasing m in the in-plane direction because of the appearance of new infinite clusters formed between layers.

The correlation length ε is a measure of characteristics of cluster-length in percolation system. When the percolation system is much thicker than ε, the system behaves like isotropic materials, and when the thickness of the percolation system is less than ε, the system would be anisotropic, whose property is related to thickness. Theoretically, the system is isotropic when $m \to \infty$ and the conductivities in all directions should have identical value. In practice, when m is large enough, the conductivities in normal and in-plane directions are independent of the layer number and $k_\perp = k| = k_1 (p - p_{c,3})^{t_3}$(where $p > p_c$ and near p_c, k_1 is the conductivity of good conductor, t is an index, subscript 3 indicates 3D, $t_3 \approx 1.6$–2.9 [7]). For limited layers, the thermal conductivity in the normal direction is [9]

$$k_\perp = k_1 \left[p_c + (p - p_c) m^{1/\upsilon_3} \right] m^{-t_3/\upsilon_3}. \tag{2}$$

The thermal conductivity in the in-plane direction is [9]

$$k| = k_1 m^{(t_2 - t_3)/\upsilon_3} (p - p_c)^{t_2} \tag{3}$$

where $t_2 = 1.3$. These equations confirm the above discussions of anisotropic conductance in thin layers of disordered composites.

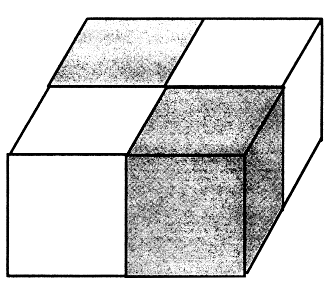

Fig. 2. A simple configuration of good and poor conductor.

2.2. Effective-medium approximation model

The coordination number is defined as the number of contacting neighbors to a given particle site or the number of the nearest neighbor bonds for a given bond. For neighboring cubic cells in Fig. 1, heat is conducted through the thermal resistance between them. Each cell has six neighboring cells and therefore there are six thermal resistors connecting adjacent cubic cell sites.

These resistors can be regarded as bonds. When the system is two-dimensional, each bond has six nearest neighbor bonds. The coordination number is six (there is no neighbor bonds on the top and bottom). When the layer number goes toward infinity, each bond has five nearest neighboring bonds at each end and the coordination number is 10. Generally, the number of the layers of the system would be finite. The average coordination number is 6–10, and could be described as

$$z = \left[6 + 10(m\text{-}1)\right]/m. \tag{4}$$

When $m = 1$, $z = 6$, it is a 2D system; when $m = 2$, $z = 8$; when $m \to \infty$, $z = 10$, it is a 3D system.

A bond resistor is formed from the contribution of neighboring cells. If the neighboring cells are both good conductor cells, the bond has a thermal conductivity of good conductor. If the neighboring cells are both poor conductor cells, the bond has a thermal conductivity of poor conductor. If one neighboring cell is good conductor and another is poor conductor, the bond has a thermal conductivity of $k_a = 2k_1k_2/(k_1 + k_2)$, which is a series connection of thermal resistance contributed from the neighboring cells. So, the system is a triple bond percolation. The probability of good conductor cell having a neighboring good conductor cell is p^2 and the probability of poor conductor cell having a neighboring poor conductor cell is $(1-p)^2$. A good conductor cell neighboring a poor conductor cell possess a probability of $2p(1-p)$. These three probabilities correspond to three kinds of bonds mentioned above. Kirkpatrick [5] developed an EMA model for binary bond percolation system. Following the procedure and treating the randomly oriented composite system as a triple bond percolation system, the in-plane thermal conductivity can be derived as

$$\begin{aligned} &p^2\frac{k_1 - k_|}{k_1 + (z/2-1)k_|} + 2p(1-p)\frac{k_a - k_|}{k_a + (z/2-1)k_|} \\ &\quad + (1-p)^2\frac{k_2 - k_|}{k_2 + (z/2-1)k_|} \\ &\quad = 0 \end{aligned} \tag{5}$$

where p is the volume percent or concentration of the good conductor cells, k_1 and k_2 are the conductivity of the good and poor conductor cells respectively, $k_|$ is the effective conductivity in the in-plane direction. The solution of Eq. (5) should satisfies $k_1 > k_| > k_2$.

The EMA method can also predict the variation of threshold concentration with layer numbers. A simple analytical result can be obtained from Eq. (5)

$$p_c = (2/z)^{0.5} \tag{6}$$

by neglecting $k_|$ and k_2. Hence, $p_c = 0.58$ for 2D percolation system, and $p_c = 0.45$ for 3D percolation system.

2.3. The computer experiments

The absence of experimental data makes it hard to compare theoretical analyses. However, computer experiments or simulations can supply thermal conductivities for the comparison.

As shown in Fig. 1, the thin layer is composed of cubic cells of good and poor conductor. A temperature gradient is applied in the normal direction for the calculation of thermal conductivity in normal direction. The control equation of conduction is discretizd on the control volume by finite difference method. Each cubic cell is treated as one control volume and the temperature at the cell center is regarded as that of the cell. The thermal resistance between adjacent cells is the addition of the contribution from each cell. The layer number in the normal direction is finite while the layer numbers in other directions are infinite. It is found that the layer effect is negligible when the layer number is beyond 20. As to observe the layer effect, the number of layers is limited below 20 in the normal direction and the numbers of layers in other direction are selected as 100. In the calculation, a random function uniformly distributed between 0 and 1 is used to attribute the conductivity of each cell. If the random number is smaller than p, this cell is a good conductor; otherwise it is a poor conductor. The temperature distribution is obtained by numerical iteration and the convergence conditions require that the temperature difference between successive iterations is smaller that 10^{-4} and the energy balance between the input and output surface is within 2%. For each concentration of good conductor, the calculations are repeated three times with different distributions of conductor cells and the effective thermal conductivity is then averaged.

Fig. 3 illustrates the numerical results of the thermal conductivity in normal direction. The conductivity decreases with increasing layer numbers no matter what the concentration of the good conductor is. The variation of thermal conductivity is notable when the layer number is smaller than 5. When $m > 10$, the conductivity approaches to a constant. When $m = 20$, the conductivity has no layer effect in the normal direction and $k_\perp = k_|$. The difference in thermal conductivities between phases has influences on the layer effect. The larger k_1/k_2 is, the more obvious the layer effect.

In Fig. 4, the variation of the effective thermal conductivity with the concentration of good conductor for a 3D system is shown. From this figure, the threshold concentration is around $p_c = 0.4$, which is consistent with the prediction of the percolation theory but is somewhat lower than prediction from simplified Eq. (6).

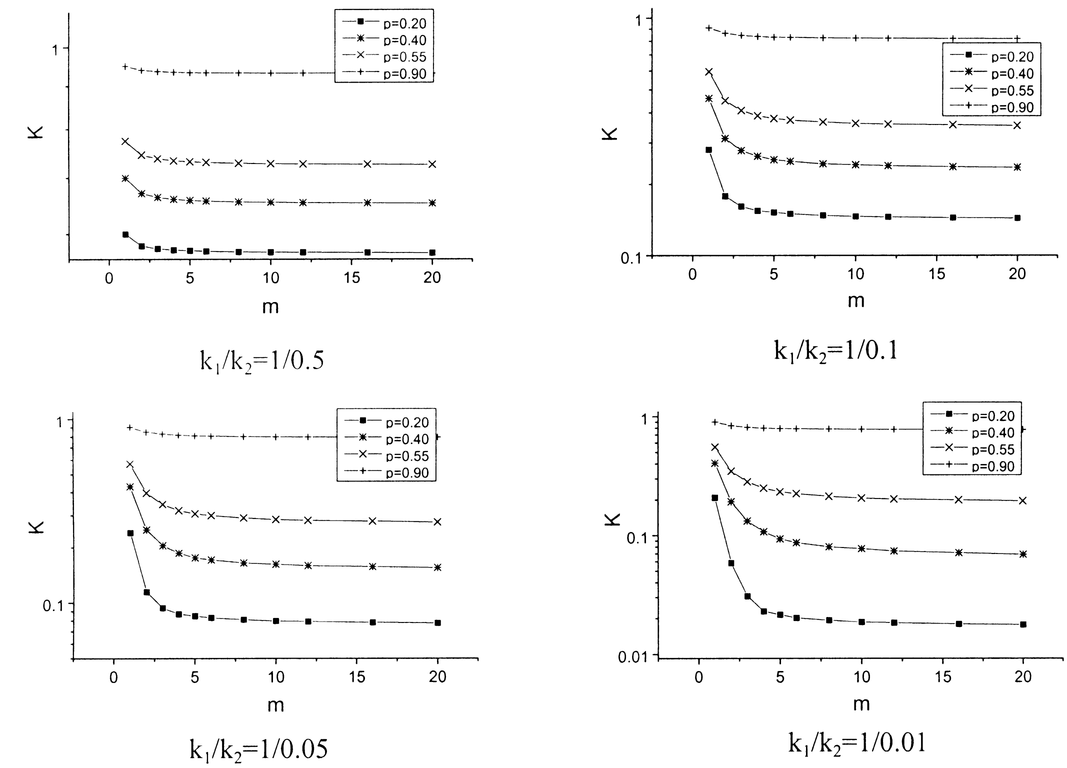

Fig. 3. The numerical result of the normalized normal thermal conductivity versus layer thickness.

The simulation of the in-plane thermal conductivity is similar to that of the normal one, with the temperature difference being applied in y-direction. Fig. 5 pictures the effective thermal conductivity in the in-plane direction as a function of layer number and the conductivity ratio of good over poor conductors. The variation of the effective thermal conductivity agrees with the prediction of EMA model and the percolation theory in trend. The in-plane conductivity grows with increasing layer thickness and is notable within layers fewer than 5. When $m > 5$, the conductivity is close to a constant. The more difference in properties of the two phases of conductors, the more significant the layer effect is. The influence of the threshold concentration can also be found in the in-plane thermal conduction. The threshold concentration declines when the system changes from 2D to 3D with increasing layer number. If the concentration of good conductor is small, such as $p = 0.2$, the conductivity is almost invariable and is close to the value of poor conductor. If the probability of good conductor is greater than the critical value, such as $p = 0.55$, the layer effect is clear. When the concentration of good conductor is nearby 100%, the effective conductivity in the in-plane direction is approximately equal to the value of good conductor and almost no layer effect exists. $k_{|} = k_{\perp}$ at m = 20, and the variation of $k_{|} \sim p$ consists with that of $k_{\perp} \sim p$.

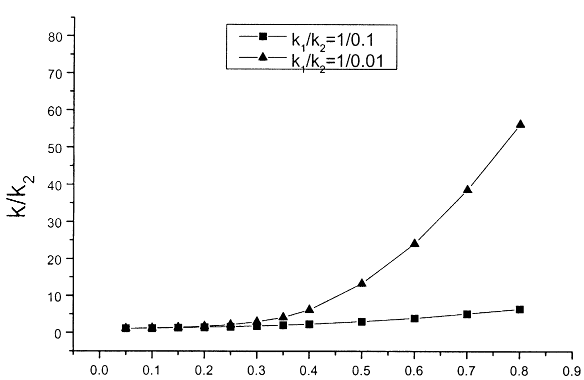

Fig. 4. The numerical simulation of the effective thermal conductivity of bulk composites versus concentration of good conductor.

The effective conductivity obtained from computer experiments is compared with EMA model in Fig. 5. The difference between the two methods is quite small at low and high concentration. At intermediate concentration, the EMA model predicts a little bit lower conductivity than the computer simulation, the maximum deviation may be up to 30%. Although the agreement

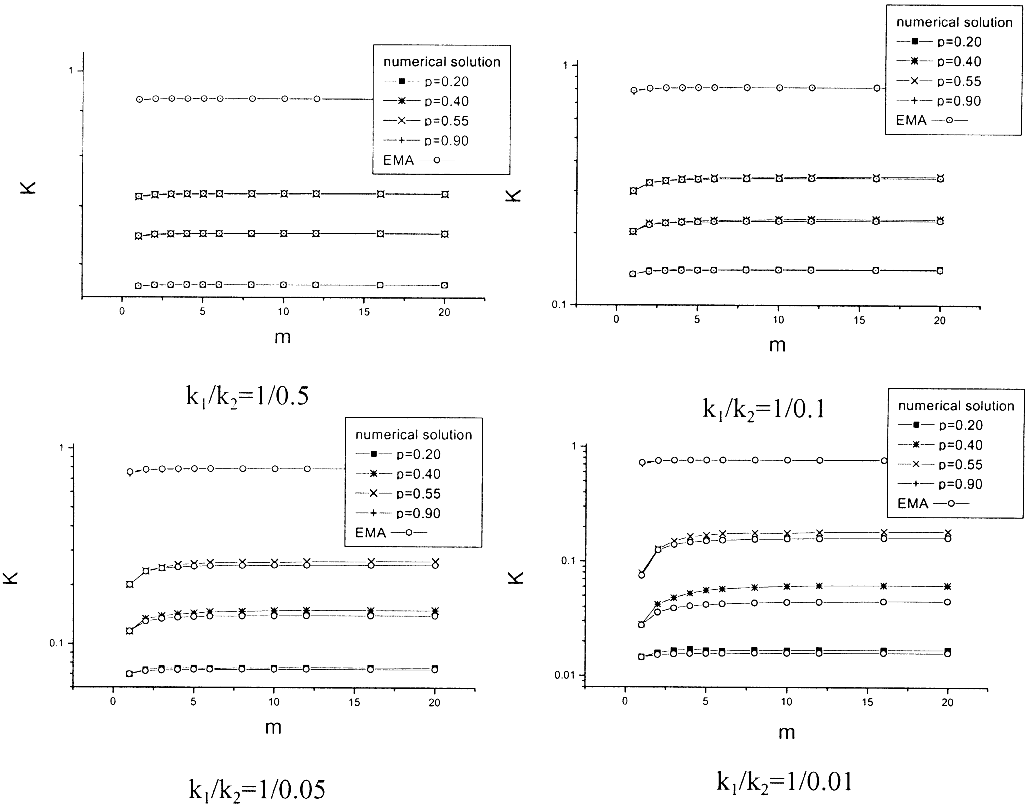

Fig. 5. The numerical result of the normalized in-plane thermal conductivity versus layer thickness and its comparison with EMA model.

is not as excellent as that was reported for a binary bond percolation system [5,6], it is still good enough for engineering applications. It is quite possible to apply Eq. (5) to predict the thermal conductivities of composites. As was found by [14], the coordination number is related to the porosity. One can compare Eq. (5) with experimental data using the coordination number z as a fitting parameter and set up a relation of the coordination number with porosity. Once this relation is determined, then Eq. (5) can predict the effective thermal conductivity of composites.

Fig. 6 shows the effective conductivity in the in-plane direction versus the concentration of good conductor for a 2D system. It is easy to determine the critical concentration for the 2D system being around 0.5.

3. Conclusion

The layer effect and the threshold concentration for randomly disordered composite material by percolation theory is analyzed, and an EMA model for the triple bond percolation system is developed and compared with computer experiments. It is found that: (1) when the layer thickness of the composite material is much larger than correlation length (the critical value), the material is homogeneous and the conductivity in the in-plane and normal directions are equal and do

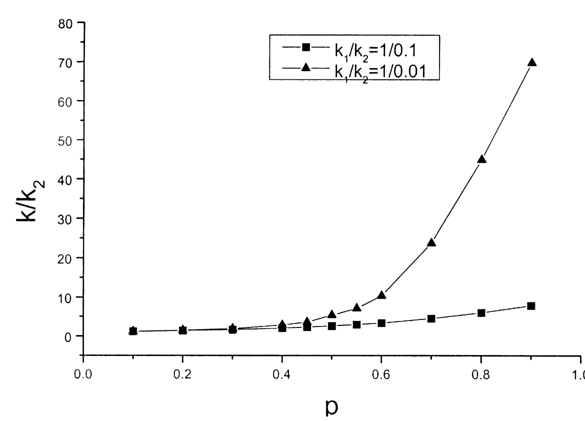

Fig. 6. The numerical simulation of the effective thermal conductivity versus concentration of good conductor for a two-dimensional percolation system.

not vary with layer thickness; (2) when the thickness is less than or nearby the correlation length, the thin layer of composites is anisotropic and the conductivity changes with the thickness. The normal thermal conductivity decreases with increasing thickness while the in-plane thermal conductivity increases. The significance of the thickness effect is influenced by the concentration of good conductor and the ratio of the conductivities of two phases in the composites, a larger conductivity ratio and an intermediate concentration will give rise to more significant thickness effect. As the layer number (that is, the ratio of the layer thickness over the characteristic size of particles) increases to beyond 20, no thickness effect exists and the layer of composite is isotropic. There is a threshold concentration of good conductor for thermal conductance of composites beyond which the conductivity increases sharply and below which the conductivity is almost a constant.

The agreement between the triple bond EMA model and computer experiments are quite satisfactory and the EMA model may be applied to predict the thermal conductivity of composite materials by using the coordination number as a fitting parameter.

Acknowledgements

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References

[1] J.L. Auriault, Effective macroscopic description for heat conduction in periodic composites, Int. J. Heat Mass Transfer 26 (1983) 861–869.

[2] L.S. Verma, A.K. Shrotriya, R. Singh, D.R. Chaudhary, Thermal conduction in two-phase materials with spherical and non-spherical inclusion, Phys. D: Appl. Phys 24 (1991) 1729/–1737.

[3] L.S. Verma, R. Singh, D.R. Chaudhary, Geometry dependent resistor model for predicting effective thermal conductivity of two phase system, Int. J. Heat Mass Transfer 37 (1994) 704–714.

[4] X.G. Liang, W.L. Qu, Effective thermal conductivity of gas-solid composite materials and the temperature difference effect at high temperature, Int. J. Heat Mass Transfer 42 (1999) 1885–1893.

[5] S. Kirkpatrick, Classical transport in disordered media: scaling and effective-medium theories, Phys. Rev. Lett 21 (1971) 1722–1725.

[6] X. Zhang, D. Stroud, Stroud, Optical and electrical properties of thin films, Phys. Rev. B 52 (1995) 2131–2137.

[7] A.V. Neimark, Electrophysical properties of a percolation layer of finite thickness, Sov. Phys. JETP 71 (1990) 341–349.

[8] P.E. Phelan, R.C. Niemann, Effective thermal conductivity of a thin, randomly oriented composite material, in: Proc. 32nd Nat. Heat Transfer Conf., Baltimore, vol. 12, 1997, pp. 145–151 (HTD-vol. 350).

[9] X. G. Liang, J.R. Lukes, C. L. Tien, Anisotropic thermal conductance in thin layers of disordered packed spheres, Proc. of 11th Int. Heat Transfer Conference, Kyongju, Korea, 1998. Heat Transfer (1998) 33–38.

[10] H. Ottavi, J.P. Clerc, G. Giraud, J. Roussenq, E. Guyan, C.D. Mitescu, Percolation process in mixtures of conducting and insulating particles, AIP Conf. Proc 40 (1978) 372–376.

[11] A.I. Maaroof, B.L. Evans, Onset of electrical conduction in Pt and Ni films, J. Appl. Phys 76 (1994) 1047–1054.

[12] D. Michels, J. Hadeler, V.J.H. Lienhard, High-heat-flux resistance heaters from VPS and HVOF thermal spraying, Experimental Heat Transfer 11 (1998) 341–359.

[13] D. Strauffer, Introduction to Percolation Theory, Taylor & Francis, London, 1985.

[14] A.L. Nayak, C.L. Tien, A statistical thermodynamic theory for coordination-number distribution and effective thermal conductivity of random packed beds, Int. J. Heat Mass Transfer 21 (1978) 669–676.