Heat conduction mechanism in silica aerogel skeleton

Z Y Luo 1,2, G H Su3, Z C Yang1,2

1 Institute of High Temperature Structural Composite Materials for Naval Ship, Naval University of Engineering, Wuhan, 430033, China;
2 College of Power Engineering, Naval University of Engineering, Wuhan, 430033, China;
3 91663 troops of the Chinese people's Liberation Army.

Abstract. In order to study the specific heat conduction process of silica aerogels, a three-dimensional random fractal skeleton model of aerogels was generated by using the diffusion-limited cluster aggregation (DLCA) method to simulate the gel process. Based on the idea of finite volume method, a numerical model of heat conduction in porous framework was established and verified. The three-dimensional temperature field and apparent thermal conductivity of the skeleton were calculated. The results show that when the initial particle concentration is 0.0764 ~ 0.191, the fractal dimension range of the skeleton model is 2.0 ~ 2.45, which is consistent with the measured value. However, in the plane perpendicular to the heat flow direction, the particle temperature is not exactly the same, which can be approximately described by normal distribution. The apparent thermal conductivity of the skeleton is three orders of magnitude lower than that of the bulk material, which can be attributed to its open network structure.

1. Introduction
Silica aerogel is a typical nanoporous material with low thermal conductivity (<0.02 W·m⁻¹·K⁻¹) [1-3]. Due to these specific properties, Silica aerogel has broad application prospects in many fields such as energy, chemical engineering, and aerospace [4, 5]. It is of great engineering value to study the internal heat transfer mechanism within the silica aerogel and find out the main factors affecting its thermo-properties. The internal heat transfer modes of aerogels are mainly gas phase heat transfer, radiation and solid phase heat conduction [6]. There have been more in-depth studies [7-11] for gas-phase heat transfer and radiation heat transfer. However there are two difficulties in the heat conduction process in the aerogel framework: One is that the three-dimensional random porous structure is very difficult to model; the other is that there is scale effect in the internal heat transfer of the primary particles which make up the skeleton.

At present, there are usually two ways to obtain the thermal conductivity of aerogel skeleton. One is to calculate the thermal conductivity of the representative unit [12, 13]. This method cannot consider the randomness of the skeleton microstructure and the accuracy of the results will be reduced. Another way is to directly obtain the scaling relationship between the thermal conductivity and density fitted by the measured results [14]. This method cannot distinguish the scale effect of primary particle heat transfer and the influence of network topology on skeleton heat transfer.

The thermal conductivity of aerogel materials was studied at the micro scale through molecular dynamics in the previous work [15, 16]. However, as a typical porous structure material, aerogel materials can not reflect the fractal characteristics of aerogel materials at the micro level due to the limitation of simulation scale. In order to further explore the heat transfer inside the aerogel
framework, in this paper, DLCA method was used to simulate the formation of aerogel. The three-dimensional temperature field of the steady-state heat conduction of the framework was obtained, and the main factors affecting the solid-phase heat conduction coefficient of aerogel were found.

2. Aerogel skeleton model

2.1. Diffusion limited cluster-cluster aggregation
In order to facilitate the convergence with the subsequent skeleton heat transfer model, the on-lattice DLCA [17] model was used to generate aerogel skeleton. In the on-lattice DLCA, the initial particles with a single particle size are randomly scattered on the three-dimensional cubic lattice points, the particle center coincides with the lattice points, and there is no overlap between the particles. The lattice size is L, and the node number is L^3. After the initialization simulation starts, randomly selected particles move along the grid. In the process of motion, when the adjacent lattice points of particles are occupied by other particles, these particles irreversibly form a group, and then the Group continues to move randomly as a whole unit. With the continuous cohesion of the group, the size of the group will be larger. When there is only one group left, the simulation is over. In the process of simulation, the rebound boundary condition is selected.

2.2. Fractal dimension of skeleton
Experimental results show that, aerogels exhibit fractal dimension within a certain range of 1.7 to 2.4 [3, 18, 19]. For the generated skeleton, the radius of rotation method is used to characterize its fractal characteristics [20, 21]. Find a point in the generated structure as the center, take R as the radius of the ball, and set the number of particles contained in the ball as N. If the skeleton has fractal characteristics, N and R should meet the following requirements:

$$N(R) \propto R^{D_f}$$

In which, $D_f$ is the fractal dimension of the skeleton.

2.3. Heat conduction model
Based on the theory of finite volume method and the law of conservation of energy, a steady-state heat transfer model of the material was established. Suppose that the energy of a particle is concentrated in the center of the particle, and the temperature within the particle is the same. The constant temperature boundary condition was used up and down of the model, and the adiabatic boundary condition was used in the circumferential direction. For the heat conduction process, there is only heat exchange between the node and its adjacent nodes. For a particle on a node, if there is no particle in a node adjacent to the particle, the adiabatic boundary condition is applied to the particle in this direction.

If there are particles in the adjacent nodes of the particles in a certain direction j, the heat exchanged between the particles in that direction is:

$$q_j = \pm k_p \frac{\pi D_p^2}{4} \left( \frac{T_i - T_p}{D_n} \right)$$

In the equation (2), kp is the thermal conductivity of the primary particle unit. Tp is the studied node temperature Dp is the diameter of primary particles, Dn is the distance between particle centers. If there is no particle in the neighboring nodes in the direction j, there is no heat exchange between particles in this direction. Finally, the linear equations about the node temperature are obtained and solved by Jacobi's over-relaxation iterative method.

3. Results and discussion

3.1 Structure characteristics
The experimental results show that the skeleton structure of aerogel exhibits fractal characteristics within a certain scale, and its fractal dimension is between 1.7-2.4 [5,19]. Fig.1(a) is the aerogel
skeleton formed by the grid scale $L$ is 50 and the particle concentration $c$ is 0.07639. Fig.1(b) is relationship between the numbers of particles in the skeleton and the radius of gyration. It can be seen that the generated skeleton structure has obvious fractal characteristics, and the fractal dimension calculated by linear fitting is 2.143.

![Skeleton model and its fractal characteristics](image)

(a) Particle distribution in the skeleton  (b) Relationship between particle number and gyration radius

Fig. 1 Skeleton model and its fractal characteristics

Fig.2 shows the change of skeleton fractal dimension with initial particle concentration. With the increase of particle concentration, the fractal dimension of skeleton fluctuates between 2.0 and 2.45, and has an increasing trend, which is consistent with the experimental results [22].Fig.3 shows the distribution of different samples with the same particle concentration $c=0.1910$. It can be seen that under the same particle concentration, the relative deviation between the distributions of different samples is very small, not more than 0.2%. Moreover, the number of particles with 1-3 adjacent particles accounts for about 90% of the total number of particles.

![Distribution of particle number with different neighboring particle](image)

Fig.2 Dependence of the skeleton FD versus the particle concentration  
Fig.3 The distribution of particle number with different neighboring particle

### 3.2. Temperature field

Fig.4 shows the skeleton model with lattice size $L$ is 20 and initial particle concentration $c$ is 0.1001. It can be seen that the node temperature distribution and the particle distribution on the node have a one-to-one correspondence. The node temperature of the existing particles lies between 300–400K, and the node temperature of the non-existing particles is 0K. Fig.5 shows the probability distribution of particle temperature in the XOY plane when $z=10$. 

![Temperature field](image)

![Probability distribution of particle temperature](image)
It can be seen that the particle temperature in the plane layer perpendicular to the heat flow direction can be approximately described by the normal distribution. The parameters of the normal distribution obtained by the fitting are $\mu=343.294$, $\sigma=19.8024$.

3.3 Skeleton thermal conductivity

Since the generated skeleton is random, its thermal conductivity is anisotropic. The thermal conductivity of a sample was taken as the average value of the calculated thermal conductivity in the directions of $x$, $y$, $z$ of that sample. Meanwhile, for each particle concentration, five samples were generated and the mean values of their thermal conductivities were taken as the skeleton thermal conductivity at this concentration. The typical diameter of the primary particle, $D_p$, is 2~6 nm. In the following calculations, $D_p=3$ nm, $D_c/D_p=0.29$, and $D_n=2.871$ nm.

3.3.1 Effects of the lattice size

It shows that when the lattice scale is too small, the calculated values of skeleton properties will be affected and scale effect will appear. According to the mechanical properties of aerogels, Hang’s calculation [16] shows that the critical size of the lattice is 60 when the initial particle concentration is 0.0764. Fig.6 shows the change of the thermal conductivity of the skeleton with the grid scale under different initial particle concentrations. It can be seen that with the increase of lattice size, the thermal conductivity decreases gradually, and the decrease is smaller and smaller. In the case of particle concentration shown in the Fig.6, the critical dimension $L_c$ is slightly larger than 60. In addition, it can be seen that with the increase of the lattice size, the fluctuation range of the thermal conductivity decreases gradually, which indicates that the randomness of the distribution of the skeleton microstructure has less influence on the results. When the scale increases to a certain extent, the skeleton can be regarded as a homogeneous material, and the thermal conductivity will not be affected by the local microstructure distribution. However, with the increase
of lattice size, the time of skeleton sample formation increases dramatically.

![Graph showing the dependence of skeleton thermal conductivity versus the lattice size under different initial particle concentration.](image)

Fig. 6 Dependence of skeleton thermal conductivity versus the lattice size under different initial particle concentration

### 3.3.2 Effects of the thermal conductivity of primary particle unit

In order to find the main reason for the extremely low thermal conductivity of the aerogel skeleton, it is calculated that the thermal conductivity $k_s$ of the skeleton varies with the thermal conductivity $k_p$ of the particle element when the skeleton shape is fixed. Table 1 shows the thermal conductivity of a skeleton sample generated when $L$ is 60 and $c$ is 0.1910, and the skeleton density $\rho$ is 249.13 kg/m$^3$. It can be seen that the thermal conductivity of the skeleton and the thermal conductivity of the particle unit meet a simple proportional relationship. Therefore, controlling the thermal conductivity between particles can effectively control the thermal conductivity of the skeleton.

| $k_p$ / W·m$^{-1}$·K$^{-1}$ | 0.50   | 1.0   | 1.4   |
|-----------------------------|--------|-------|-------|
| $k_s$ / W·m$^{-1}$·K$^{-1}$ | 1.09×10$^{-3}$ | 2.18×10$^{-3}$ | 3.05×10$^{-3}$ |

The typical thermal conductivity of bulk amorphous silica is 1.4 W·m$^{-1}$·K$^{-1}$. In fact, due to the existence of interfacial thermal resistance at the interface of particles, the thermal conductivity $k_p$ between particles is smaller than that of bulk materials [23]. It can be seen that the calculated thermal conductivity is nearly three orders of magnitude smaller than the thermal conductivity of bulk material, while the bone frame density is only one order of magnitude lower than the typical density of bulk material. This indicates that the reason why the thermal conductivity of aerogel solid skeleton is very low is mainly due to its special open network structure.

### 3.3.3 Effects of the branch particles

From Fig. 2 (a), some particles are located on the "branches" protruding from the skeleton, not on the heat conduction path from the heat source to the cold source. About 20% of the particles in the skeleton have only one adjacent particle. Except for a few particles close to the heat source or cold source, the rest are all on the "branches" of the skeleton. In order to study the influence of "branch" particles on the thermal conductivity of skeleton, the thermal conductivity of skeleton after deleting some "branch" particles is calculated and compared with that before deleting. In this paper, only the particles with one adjacent particle (excluding the particles near the heat source or cold source) are deleted. Because each time a particle is deleted, a new branch particle with only one adjacent particle may be generated, so the program deletes the generated skeleton in multiple rounds. Fig.7 (a) and (b) are skeleton models before and after deleting some branch particles. The total number of skeleton particles before deletion is 917, and the total number of skeleton particles after deletion is 611. Take $k_p = 1$ W·m$^{-1}$·K$^{-1}$, the calculated thermal conductivity of the skeleton before and after are both 0.0013 W·m$^{-1}$·K$^{-1}$. This shows that the existence of "branch" particles has no effect on the heat transfer of the skeleton, that is to say, only some particles in the heat conduction path contribute to the heat conduction of the skeleton. This is one of the most important
reasons why the thermal conductivity of aerogel skeleton is very low.

4. Conclusions
In this paper, the skeleton model of aerogel was generated, and the internal heat transfer process was studied by numerical method. The following conclusions are obtained.

(1) Using the DLCA model to simulate the gel process, a more realistic three-dimensional random fractal skeleton model of aerogels was generated. The results show that when the initial particle concentration increases from 0.0764 to 0.1910, the fractal dimension of skeleton fluctuates between 2.0 and 2.45, which is in good agreement with the experimental results.

(2) Based on the idea of finite volume method, the numerical heat transfer model of particle porous materials was established according to the conservation of energy. Combined with the generated skeleton model and the numerical heat transfer model, the three-dimensional temperature field in steady state heat conduction in aerogel was reconstructed. The results show that the temperature of particles in the skeleton decreases gradually along the direction of heat flow, but in the plane perpendicular to the direction of heat flow, the temperature is not the same, so it can be approximately described by normal distribution.

(3) The influence of thermal conductivity of particle element and topological structure of skeleton on apparent thermal conductivity of skeleton was analyzed. The results show that the reason why the thermal conductivity of aerogel skeleton is very low is mainly due to its special open network structure. The specific reasons can be attributed to not all skeleton particles contribute to heat conduction.

Acknowledgements
This work was supported by the National Natural Science Foundation of China (Grant No. 51702364) and Independent Project of Naval University of Engineering, China (Grant No. 425517K152).

References
[1] Dorcheh A S, Abbasi M H 2008 Journal of Materials Processing Technology 199 10
[2] Fricke J, Heinemann U, Ebert H P 2008 Vacuum 82 680
[3] Aegerter MA, Leventis N, Koebel MM 2011 Aerogels Handbook. (New York: Springer-Verlag)pp 585-606.
[4] Lee OJ, Lee KH, Yim TJ et al 2002 Journal of Non-Crystalline Solids 298 287
[5] Zeng SQ, Hunt A, Greif R 1995 Journal of Non-Crystalline Solids 186 264
[6] JJ Zhao, YY Duan, XD Wang et al 2012 Int J Heat Mass Transfer 55 5196
[7] XD Wang, D Sun, YY Duan, ZJ Hu 2013 J Non-Cryst Solids 375 31
[8] JJ Zhao, YY Duan, XD Wang 2013 Int J Therm Sci 70 54
[9] SQ Zeng, A Hunt, R Greif 1995 J Heat Transfer 117 1055
[10] GS Wei, XX Zhang, F Yu 2008 J University of Science and Technology Beijing 30 781
[11] GS Wei, YS Liu, XX Zhang 2011 Int J Heat Mass Transfer 54 2355
[12] Feng YJ, Yu BM, Zou MQ 2004 J Porous Media 10 551
[13] R Coquard, D Baillis, V Grigorova 2013 J Non-Cryst Solids 363 103.
[14] A Hasmy, R Jullien 1995 J Non-Cryst Solids 186 342
[15] ZY Luo, ZC Yang, ZF Fei 2018 Journal of Aerospace Power 6 1363
[16] Yang ZC, Su GH, Chen B 2016 COMPUTERS MATERIALS & CONTINUA, 51 43
[17] SM Hang, PR Anthony, HP Jean 2000 J Non-Cryst Solids 277 127
[18] YI Aristov, N Lisitsa, VI Zaikovski 1996 React Kinet Catal Lett 58 367
[19] H Anwar, F Marie, A Eric 1995 J Non-Cryst Solids 186 118
[20] M Kolb, R Botet, R Jullien 1983 Phys Rev Lett 51 1123
[21] JZ Zhang 2011 Fractals. (Beijing: Tsinghua University Press) p 217
[22] WQ Tao 2001 Numerical Heat Tranfer. (Xi’an: Xian Jiaotong Universiy Press) p 34
[23] C Bi, GH Tang 2013 Int J Heat Mass Transfer 64 452