

Theoretical study on the effective thermal conductivity of silica aerogels based on a cross-aligned and cubic pore model

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SPECIAL TOPIC — Heat conduction and its related interdisciplinary areas

Theoretical study on the effective thermal conductivity of silica aerogels based on a cross-aligned and cubic pore model

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Aerogel nanoporous materials possess high porosity, high specific surface area, and extremely low density due to their unique nanoscale network structure. Moreover, their effective thermal conductivity is very low, making them a new type of lightweight and highly efficient nanoscale super-insulating material. However, prediction of their effective thermal conductivity is challenging due to their uneven pore size distribution. To investigate the internal heat transfer mechanism of aerogel nanoporous materials, this study constructed a cross-aligned and cubic pore model (CACPM) based on the actual pore arrangement of SiO_2 aerogel. Based on the established CACPM, the effective thermal conductivity expression for the aerogel was derived by simultaneously considering gas-phase heat conduction, solid-phase heat conduction, and radiative heat transfer. The derived expression was then compared with available experimental data and the Wei structure model. The results indicate that, according to the model established in this study for the derived thermal conductivity formula of silica aerogel, for powdery silica aerogel under the conditions of $T = 298$ K, $a_2 = 0.85$, $D_1 = 90$ μm, $\rho = 128$ kg/m^3, within the pressure range of 0–10^5 Pa, the average deviation between the calculated values and experimental values is 10.51%. In the pressure range of 10^3–10^4 Pa, the deviation between calculated values and experimental values is within 4%. Under these conditions, the model has certain reference value in engineering verification. This study also makes a certain contribution to the research of aerogel thermal conductivity heat transfer models and calculation formulae.

Keywords: silica aerogel, effective thermal conductivity, two pore-size structure model, porous medium heat transfer

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1. Introduction

An aerogel is a solid material with a nano-porous network structure filled with a gaseous dispersed medium in its pores. Due to its unique microstructure, it holds 15 Guinness World Records for solid materials, including the lowest thermal conductivity (0.012–0.016 W/m·K), lowest density (0.16 mg/cm^3), lowest dielectric constant (< 1.003), highest acoustic impedance (106 kg/(m^2·s)), and highest porosity ($> 99.9\%$).[1,2] The critical electrical components and wiring of China's first Mars rover, Tianwen-1, as well as China's Zhurong rover, and the American Mars rovers, Spirit and Opportunity, all use aerogel protection to withstand temperatures as low as -100 °C.[3]

The main reasons for the extremely low thermal conductivity of aerogels are twofold: the first is the high porosity of aerogels, with the porosity of silica aerogels ranging from 90% to 99%, and the volume fraction of air being as high as approximately 99.8%.[4] Heat transfer within aerogels mainly occurs through the air, and the thermal conductivity of air in standard conditions is 0.024 (W/(m·K)); the second reason is the restriction on the thermal motion of gas molecules. The pore size of aerogels is smaller than the average free path of air molecules, which is approximately 70 nm in standard conditions, while the pore size distribution of silica aerogels ranges from 2 nm to 50 nm.[5] The silica aerogel framework significantly inhibits the thermal motion of air molecules, reducing the thermal conductivity of air, resulting in the thermal conductivity of aerogels being lower than that of air, with a value of only 0.018 (W/(m·K)) under standard conditions. These two factors combine to create the ultra-low thermal conductivity of aerogels.

The competition in the aerogel market is becoming increasingly fierce, prompting aerogel production companies to continuously launch aerogel products with better performance and lower cost. The development of new products relies on research into the effective thermal conductivity of aerogels. Conducting theoretical research on the effective thermal conductivity of aerogels helps to identify the reasons for the low thermal conductivity of aerogels, leading to improvements in the performance of aerogel products. The theoretical research on the effective thermal conductivity of aerogels makes the engineering application of aerogels more convenient. In engineering applications, it is necessary to calculate the thickness of the required thermal insulation material based on in-

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sulation or cooling requirements. If aerogel is chosen as the thermal insulation material, the effective thermal conductivity of aerogels is needed to determine the thickness of the required aerogel material. More importantly, research on the effective thermal conductivity of aerogels contributes to the exploration of heat transfer mechanisms in nanoscale porous materials, with significance for the development of nanoscale foundational theories.

To promote the development and application of aerogels, scientists have conducted extensive research on the heat transfer mechanisms and effective thermal conductivity calculation of aerogels. Zeng[6] proposed three structural models based on the microstructure of aerogels: the crossed-bar model, crossed-cylindrical model, and cubic array model composed of nanospheres, as shown in Fig. 1. Among the three models, only the cubic array model composed of nanospheres yielded satisfactory computational results and found broader applications. However, it only considers the heat transfer between the gas phase and solid phase of aerogels, neglecting the radiation heat transfer of aerogels. Building upon previous research, Yichang[7] modified Zeng's[6] cross-linked rod model to hexagonal and octagonal prisms based on the observed particle shapes and arrangements under scanning electron microscopy. The variations in effective thermal conductivity under different parameters for several structural models were analyzed; however, the radiation heat transfer of aerogels was not investigated.

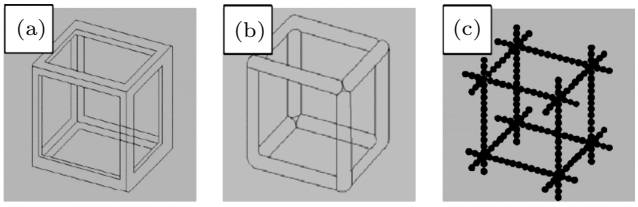


Fig. 1. Zeng's models[6] ((a) crossed-bar model; (b) crossed-cylindrical model; (c) cubic array model composed of nanospheres).

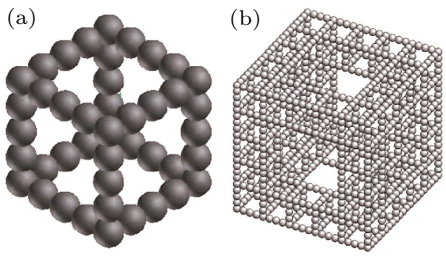


Fig. 2. The fractal crossed-sphere-rod model: (a) first-level structure, (b) second-level structure.[9]

Good *et al.*[8] discovered that small-scale structures in aerogels can transition fractally to larger-scale structures. Building upon this, Xie[9] proposed a fractal cross-linked sphere-rod model, as depicted in Fig. 2, and compared its computational results with the experimental results of Wei.[10] The study found that the computed values of effective thermal conductivity at different densities are generally lower than the experimental values, and the calculations involve multiple integrations, making the computation relatively complex.

Dan,[11] integrating the microstructure of aerogels, proposed a hollow-sphere cubic structure model based on the cubic array model composed of nanospheres, as shown in Fig. 3. Compared with previous models, this model exhibits smaller errors between predicted values and experimental values, and does not require any empirical parameters. In comparison with Zeng's model,[6] the computational accuracy is improved. However, this model only investigates the thermal conduction principles of aerogels under a single-scale aperture.

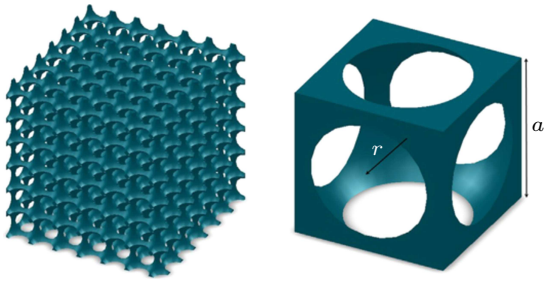


Fig. 3. The hollow spherical cube structure model.[11]

Wei[10] discovered, via electron microscopy, that powdered SiO2 aerogels possess both nano-scale and micrometer-scale pores. Based on the cubic array model composed of nanospheres, they established two different particle size periodic filling models, as shown in Fig. 4. The model proposed by Wei *et al.*[10] considers the dual-scale porosity of aerogels. However, the formula for the gas–solid coupled thermal conductivity coefficient used in the calculation process is derived from composite aerogels, which theoretically may not be fully adequate for pure silica aerogels.

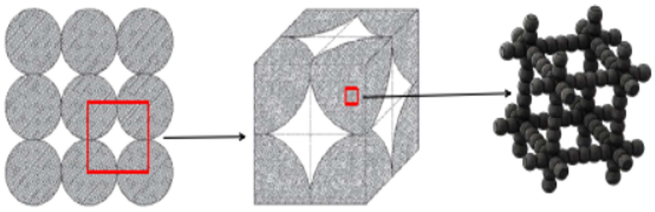


Fig. 4. The spherical structural model of nanometer-sized pores with face-to-face contact and their unit cell.[10]

In the 21st century, with full recognition of the importance of aerogel materials, scientists have been exploring various heat transfer models for aerogel materials. However, there are still some shortcomings in model development and data validation. Firstly, there are currently relatively few established dual-scale aperture models, and the most suitable dual-scale aperture model for silica aerogels has not been found yet. Secondly, the derived calculation formulas suffer from insufficient validation data and limited validation scope, which fail

to fully reflect the applicability of the models and formulas. This paper aims to address the above issues by establishing a new dual-scale aperture model for aerogels and collecting over a hundred sets of data under different conditions to validate the thermal conductivity calculation formula derived from this model. It further explores the most suitable model and calculation formula for calculating the effective thermal conductivity of aerogels. Due to the widespread application of silica aerogels, they are selected as the research subject in this paper.

2. Establishment of the heat transfer model

According to scanning electron microscope images at different magnifications of aerogels, it is evident that silica aerogels initially aggregate from nano-scale frameworks into micrometer-sized particles, which are then further stacked to form structures at the micrometer level. These two structure levels result in two levels of pore sizes, as shown in Fig. 5.[12] By combining the real structure of aerogels, shown in scanning electron microscope images, and aiming to derive a simpler thermal conductivity calculation formula with higher applicability for future optimization, we have established a dual-scale pore periodicity model, denoted as the cross-aligned and cubic pore model (CACPM).

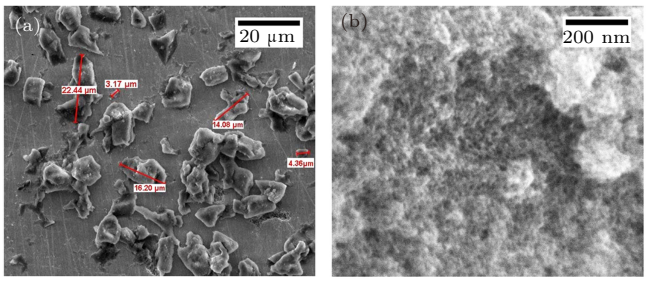


Fig. 5. (a) SEM micrographs of the aerogel powder dissolved in ethanol, (b) an SEM micrograph of the aerogel particles' surface.[12]

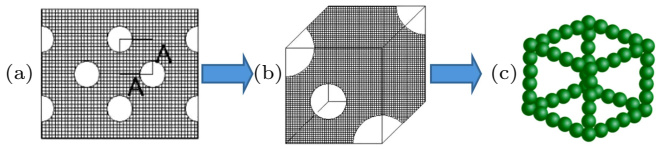


Fig. 6. The cross-aligned and cubic pore model (CACPM): (a) the plan view of the model; (b) a cubic unit structure; (c) the cubic array structure model.

The CACPM is depicted in Fig. 6, where both Figs. 6(a) and 6(b) represent the micrometer-scale structures of the model, corresponding to the secondary particle portion of the model. Figure 6(a) illustrates the plan view of the model, while Fig. 6(b) displays a cubic unit structure extracted from the model with side length A. The transparent spherical regions represent the pores of the secondary particles, arranged in a crossing pattern with a diameter of D_1. The grey regions depict the solid skeleton structure of the secondary particles composed of primary particles, as illustrated in Fig. 6(c). Figure 6(c) illustrates the nanometer-scale structure of the model, referred to as the cubic array model composed of nanospheres, initially invented by Zeng, as the primary particles of the model under study in this paper. The green spheres denote the solid skeleton structure of the primary particles, while the remaining portions are filled with gas.

3. The derivation of the formula for calculation of thermal conductivity

The pore size of silica aerogel ranges from 2 nm to 50 nm, which is smaller than the mean free path of air molecules under standard conditions (70 nm), making the macroscopic thermal conductivity calculation formula inapplicable. Therefore, it is necessary to employ kinetic theory to study the thermal motion of gas molecules and subsequently calculate the gas-phase thermal conductivity of aerogels. This paper adopts kinetic theory to calculate the gas-phase thermal conductivity of aerogels and derives the final thermal conductivity formula using Fourier's law.

All pressures used in the calculations in this article are relative to atmospheric pressure. Assuming a cube with side length A as the heat transfer unit model, as shown in Fig. 7, heat transfer occurs as a one-dimensional steady-state process with heat flowing downward. The temperature difference between the top and bottom of the heat transfer unit model is denoted as T, and the total heat flow is denoted as Q. Q consists of two parts, where Q_1 represents the gas–solid coupled heat flow passing through the micrometer-scale spherical pores and the solid skeleton, and Q_2 represents the heat flow passing only through the solid skeleton.

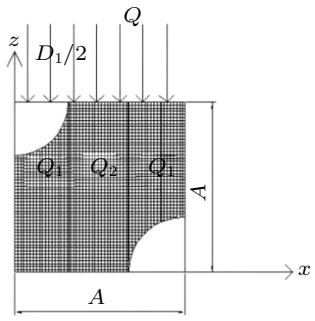


Fig. 7. Heat transfer within the unit cell structure.

According to Fourier's law, the formulas for calculating Q_1 and Q_2 can be derived. The formulas obtained are as follows:

$$\begin{aligned} Q_1 &= \int_0^{\frac{D_1}{2}} \frac{2\pi x \Delta T}{\frac{\sqrt{\left(\frac{D_1}{2}\right)^2 - x^2}}{k_{g1}} + \frac{A - \sqrt{\left(\frac{D_1}{2}\right)^2 - x^2}}{k_n}} \cdot \mathrm{d}x \\ &= \frac{\pi D_1 \Delta T k_n}{\mu^2} \left(\mu + \frac{2A}{D_1} \ln \frac{2A}{\mu D_1 + 2A} \right), \qquad (1) \\ Q_2 &= \frac{\left(A^2 - \pi \times \left(\frac{D_1}{2}\right)^2 \right) \times \Delta T}{A/k_n} \end{aligned}$$

$$= \left(A - \frac{\pi D_1^2}{4A}\right) \cdot k_{\mathrm{n}} \cdot \Delta T, \tag{2}$$

where D_1 is the diameter of spherical pores; A is the side length of the unit cell structure; $\mu = k_{\mathrm{n}}/k_{\mathrm{g1}} - 1$; k_{n} is the gas–solid coupled thermal conductivity of primary particles; and k_{g1} is the gas-phase thermal conductivity within the pores of secondary particles.

The gas–solid coupled thermal conductivity of secondary particles is k_{e}, and according to Fourier's law, the expression for the total heat flow Q of the unit cell structure model can be obtained as follows:

$$Q = \frac{\Delta T \cdot A^2}{A/k_{\mathrm{e}}} = \Delta T \cdot A \cdot k_{\mathrm{e}}, \tag{3}$$

$$Q = Q_1 + Q_2, \tag{4}$$

$$k_{\mathrm{e}} = \frac{Q_1 + Q_2}{\Delta T A} = \frac{\pi \delta k_{\mathrm{n}}}{\mu^2}\left(\mu + \frac{2}{\delta}\ln\frac{2}{\mu\delta + 2}\right) + k_{\mathrm{n}}\left(1 - \frac{\pi\delta^2}{4}\right), \tag{5}$$

where $\delta = D_1/A$, $0 \le \delta \le 1$.

Based on the above formula, the relationship between k_{e}, k_{n}, and k_{g1}can be obtained. However, to obtain k_{e}, it is necessary to calculate k_{n} and k_{g1} as well.

To calculate the gas–solid coupled thermal conductivity k_{n} of primary particles, we compute it using the cubic array model composed of nanospheres. This model and its internal heat transfer model are illustrated in Fig. 8.

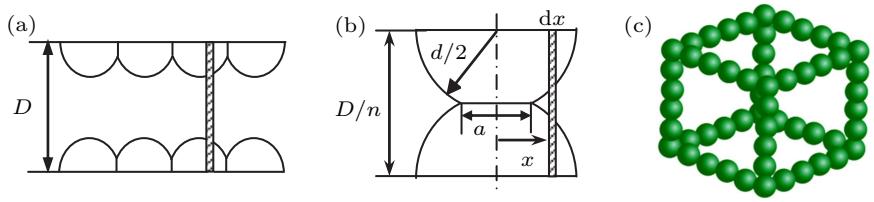


Fig. 8. The cube array structure model and internal heat transfer of the unit cell. (a) A schematic diagram of sphere–surface contact (Q_1); (b) the corresponding diagram of sphere space (Q_2); (c) the cube array structure model (Q_3).

$$Q_1 = \int_{\frac{a}{2}}^{\frac{d}{2}} \frac{(\Delta T/n)\,2\pi x \mathrm{d}x}{2\sqrt{(d/2)^2 - x^2}/k_{\mathrm{s}} + \left[D/n - 2\sqrt{(d/2)^2 - x^2}\right]/k_{\mathrm{g2}}} + \frac{\pi\left(\frac{a}{2}\right)^2 \Delta T k_{\mathrm{s}}}{D}$$
$$= -\frac{\pi\Delta T\,\mathrm{d}k_{\mathrm{g2}}}{2n\beta}\left[\frac{D}{nd\beta}\ln\left(1 - \frac{nd\beta}{D}\sqrt{1 - \left(\frac{a}{d}\right)^2}\right) + \sqrt{1 - \left(\frac{a}{d}\right)^2}\right] + \frac{1}{4}\pi a^2 \Delta T k_{\mathrm{s}}/D, \tag{6}$$

$$Q_2 = \int_0^{\sqrt{(d/2)^2 - (a/2)^2}} \frac{2(n-1)\Delta T 2\pi x \mathrm{d}x}{2\frac{\sqrt{(d/2)^2 - x^2}}{k_{\mathrm{s}}} + \frac{D - 2\sqrt{(d/2)^2 - x^2}}{k_{\mathrm{g2}}}} = \frac{\pi(n-1)\Delta T d}{\beta} k_{\mathrm{g2}}\left(\frac{a}{d} - 1 + \frac{D}{\beta d}\ln\frac{D - \beta a}{D - \beta d}\right), \tag{7}$$

$$Q_3 = \frac{(D-d)^2 \Delta T k_{\mathrm{g2}}}{D}, \tag{8}$$

where k_{s} is the solid thermal conductivity in the cube array structure model; k_{g2} is the gas phase thermal conductivity in the cube array structure model; $\beta = 1 - k_{\mathrm{g2}}/k_{\mathrm{s}}$; d is the diameter of the small sphere; D is the side length of the cube array structure model; a is the diameter of the contact surface between two small spheres; n is the number of small spheres on each side of the cube array structure model; ΔT is the temperature difference between the bottom and top of the cube array structure model.

Starting from the overall structure model, according to Fourier's law, the expression for the total heat flow Q of the cubic array structure model composed of nano balls can be obtained as

$$Q = \frac{\Delta T \cdot D^2}{D/k_{\mathrm{n}}} = \Delta T \cdot D \cdot k_{\mathrm{n}}, \tag{9}$$

$$Q = Q_1 + Q_2 + Q_3. \tag{10}$$

Therefore, the effective thermal conductivity k_{n} of SiO_2 aerogel nanoparticles can be obtained from the following equation:

$$k_{\mathrm{n}} = \frac{Q_1 + Q_2 + Q_3}{\Delta T D}. \tag{11}$$

By substituting Q_1, Q_2, and Q_3 derived from the previous text into the above equation, and letting $d = \sqrt{a^2 + (D/n)^2}$, the following can be obtained:

$$k_{\mathrm{n}} = \left\{\frac{\pi a_1^2 a_2^2}{4(1-\beta)} + \left(1 - a_1^2\right) - \frac{\pi a_1^2\left(1 - a_2^2\right)}{2\beta^2} \times \left[\beta + \ln(1-\beta)\right] + \frac{\pi}{\beta}\left(1/\sqrt{1 - a_2^2} - a_1\right) \times \left[\frac{1}{\beta a_1}\ln\frac{1 - \beta a_1 a_2}{1 - \beta a_1} - (1 - a_2)\right]\right\} \cdot k_{\mathrm{g2}}, \tag{12}$$

where $a_1 = d/D$, $a_2 = a/d$.

To obtain the gas–solid coupled thermal conductivity k_n of primary particles, we need to know the gas-phase thermal conductivity k_{g2} in the cubic array structure model, and the solid thermal conductivity k_s in the cubic lattice structure model.

Zeng[13] *et al.* obtained the expression for the gas-phase thermal conductivity at the nanoscale by further considering the influence of material microstructure parameters and combining with the non-equilibrium transport theory of molecular dynamics for gas molecules in aerogel

$$k_{g2} = \frac{60.22\times10^5 PT^{-0.5}}{0.25S_s\rho_{por}\varepsilon_1^{-1}+4.01\times10^9 PT^{-1}}. \tag{13}$$

Here, S_s is the specific surface area of the aerogel, which can be measured via a low-temperature nitrogen adsorption method; ρ_{por} is the density of the aerogel material particles, with the expression of $\rho_{por}=\rho/(1-\varepsilon)$, where ρ is the overall density of the aerogel material stacking, and ε is the porosity of the aerogel; ε_1 is the porosity of the cubic array structure model, with the expression of $\varepsilon_1 = 1-\rho_{por}/\rho_{bulk}$, where ρ_{bulk} represents the density of the base material (for SiO_2 aerogel $\rho_{bulk}=2200$ kg/m^3); P refers to the pressure of the test environment gases; and T is the absolute temperature.

The specific surface area S_s is directly related to the density and micro-porous structure of the aerogel. According to the cubic array unit structure composed of nanoparticles, the specific surface area S_s and porosity ε_1 of the material can be calculated as follows:

$$S_s = \frac{\pi d\left(3D-2d\sqrt{1-a_2^2}\right)}{\rho_{por}D^3}, \tag{14}$$

$$\varepsilon_1 = 1-\frac{\pi\left(a^2+2d^2\right)\left(3D-2\sqrt{d^2-a^2}\right)}{12D^3}. \tag{15}$$

After organization, the following formula can be obtained:

$$d = \frac{12(1-\varepsilon_1)}{\left(2+a_2^2\right)\rho_{por}S_s}, \tag{16}$$

$$D^3 - \frac{3\pi d}{\rho_{por}S_s}D + \frac{2\pi\sqrt{1-a_2^2}d^2}{\rho_{por}S_s} = 0. \tag{17}$$

The density and specific surface area of aerogel can be measured; therefore, the structural parameters d and D can be directly calculated from the above two formulas.

For the calculation of the solid-phase thermal conductivity of aerogels, the main heat transfer mechanism in the solid-phase of the material is achieved through phonon or local lattice vibrations. Due to the nanometer-scale thickness of the solid skeleton in the material, the phonon motion in the material is restricted by the solid boundary; therefore, there is a size effect on the solid-phase thermal conductivity of aerogels. Chen *et al.*[14] discovered that the solid-phase heat transfer of particles at the nanoscale has the characteristics of non-equilibrium and non-locality when solving the Boltzmann transport equation. When the radius of the nanoscale particle is close to the average free path of phonons, the heat transfer rate of the nanoscale particle will significantly decrease, resulting in a much higher temperature rise in the nanoscale particle than predicted by Fourier's law of heat conduction. According to a series of research, Chen *et al.*[14] proposed a formula to calculate the solid-phase thermal conductivity

$$k_s = \frac{3r^*}{3r^*+4}k_{bulk}. \tag{18}$$

Here, r^* is the dimensionless radius of the nanoscale particle, $r^* = r/l_s$; and l_s is the average free path of phonons in the solid material. For SiO_2 aerogels, $l_s = 0.58$ nm. Here, r is the radius of the nanoscale particle, that is, $r = d/2$. Meanwhile, k_{bulk} is the thermal conductivity of bulk SiO_2 aerogel materials, which can be calculated using the following fitting equation:[15]

$$\begin{aligned} k_{bulk} &= 7.5264\times10^{-1}+3.13\times10^{-3}T \\ &\quad -4.5242\times10^{-6}T^2+3.5253\times10^{-9}T^3. \end{aligned} \tag{19}$$

According to molecular theory, thermal conduction in gases is due to the collisions between gas molecules during molecular thermal motion. When high-speed ("hot-side") molecules collide with low-speed ("cold-side") molecules, energy is transferred to the low-speed molecule, resulting in heat transfer. Molecular theory is a theory that explains the laws of thermal phenomena from the perspective of the microstructure of matter and is more suitable for the analysis of heat transfer processes at a microscopic scale. In this study, the Kaganer model based on the Knudsen number was used to calculate the gas-phase thermal conductivity k_{g1} in the large pores. This model is generally considered to be applicable to micropores with a diameter greater than 10 μm microns and macroscopic large pores:[16]

$$k_{g1} = \frac{k_{g,0}\cdot\varepsilon_m}{(1+2\beta Kn)}, \tag{20}$$

$$\beta = \frac{2\gamma}{\gamma+1}\cdot\frac{1}{Pr}\cdot\frac{2-\alpha_1}{\alpha_1}. \tag{21}$$

Here, $k_{g,0}$ is the thermal conductivity of gas in free space, for air, $k_{g,0} = 1.489\times10^{-3}T^{0.5}$;[13] ε_m is the porosity of the material's large pores; γ is the adiabatic index of the gas; Pr is the Prandtl number; and α_1 is the energy adjustment coefficient. For air in aerogels, the coefficient $\beta\approx2$; Kn is the Knudsen number, which is the ratio of the mean free path of gas molecules l_0 to the average pore diameter D_m, and in the CACPM, the average pore diameter $D_m = D_1$:

$$Kn = \frac{l_0}{D_m}, \tag{22}$$

$$l_g = \frac{k_B T}{\sqrt{2}\pi p d_g^2}. \tag{23}$$

Here, Boltzmann's constant $k_B = 1.38 \times 10^{-23}$ J/K; T is the thermodynamic temperature; p refers to the pressure of the test environment gases; d_g is the diameter of gas molecules and, for air, $d_g = 3.53 \times 10^{-10}$ m.

In the calculation of the radiative thermal conductivity of SiO_2 aerogel, in practical applications, the optical thickness of the thermal insulation material is generally large (i.e., $\tau \geq 1$); therefore, the diffusion approximation model can be used. The radiative heat transfer inside the aerogel material belongs to medium radiation. In general engineering applications, it is assumed to satisfy the optical thick medium hypothesis and the Rosseland equation can be used to calculate the material's radiative thermal conductivity.[17] The calculation formula is shown below:

$$q(x) = -\frac{16}{3\rho\sigma_{e,R}} n^2 \sigma T^3 \frac{\partial T}{\partial x}. \tag{24}$$

Furthermore, the expression for radiative thermal conductivity can be derived as follows:

$$k_r = \frac{16n^2\sigma}{3\rho\sigma_{e,R}} T^3, \tag{25}$$

where n is the shading coefficient, which is approximately 1 for SiO_2 aerogel; σ is the Boltzmann constant, $\sigma = 5.67 \times 10^{-8}$ W·m^{-2}·K^{-4}; ρ is the material density; and $\sigma_{e,R}$ is the Stefan–Boltzmann mean extinction coefficient, which can be obtained using the following equation:

$$\sigma_{e,R} = \frac{1}{\int_0^\infty \frac{1}{\sigma_{\lambda,m}} \cdot \frac{\partial e_{b\lambda}}{\partial e_b} \mathrm{d}\lambda}. \tag{26}$$

Here, e_b is the blackbody radiance, $e_{b\lambda}$ is the blackbody spectral radiance, and $\sigma_{\lambda,m}$ is the material's mass spectral attenuation coefficient, which can be measured through experiments. This article uses the experimental data from Wei[10] to calculate $\sigma_{\lambda,m}$ and thus obtain $\sigma_{e,R}$ as well as the radiative thermal conductivity of SiO_2 aerogel material.

The model established in this paper is a dual-scale pore model. The primary particles are at the nanoscale and are modeled using a cubic array structure, as depicted in the heat transfer model shown in Fig. 8. Due to the difficulty in representing pore sizes in the cubic model, as shown in formula (6), we use the parameters of the small sphere diameter (d), the side length of the cubic array structure (D), and the contact diameter (a) for size calculations when computing heat transfer in the cubic model. The secondary particles are at the microscale and have a cross-arrangement pore structure, as shown in Fig. 7. The pores in the secondary particles are spherical, and the use of pore diameter for size representation is more convenient. Therefore, for the heat transfer calculation of secondary particles, we use the pore diameter (D_1) as the size calculation parameter, as shown in formula (1).

By organizing the heat transfer calculation expressions mentioned above, the overall effective thermal conductivity of SiO_2 aerogel nanoporous material can be obtained as the sum of the gas–solid coupling thermal conductivity and the radiative thermal conductivity in the unit cell structural model:

$$k = k_e + k_r = \frac{\pi\delta k_n}{\mu^2}\left(\mu + \frac{2}{\delta}\ln\frac{2}{\mu\delta+2}\right) + k_n\left(1 - \frac{\pi\delta^2}{4}\right) + \frac{16n^2\sigma}{3\rho\sigma_{e,R}} T^3. \tag{27}$$

4. Verification and comparison of calculation formulas

To verify the effectiveness of the cross-aligned and cubic pore model (CACPM), we compared the calculated results of this model with experimental data on the effective thermal conductivity of SiO_2 aerogels at different densities as a function of pressure. We compared it with the results obtained from the Wei[18] structural model under the same conditions, to explore the applicability of the derived formula for effective thermal conductivity.

According to Wei,[18] the relevant calculation parameters selected are as follows: temperature $T = 298$ K, $a_2 = 0.85$, and the diameter of spherical large pores in the powder SiO_2 aerogel is $D_1 = 90$ μm.

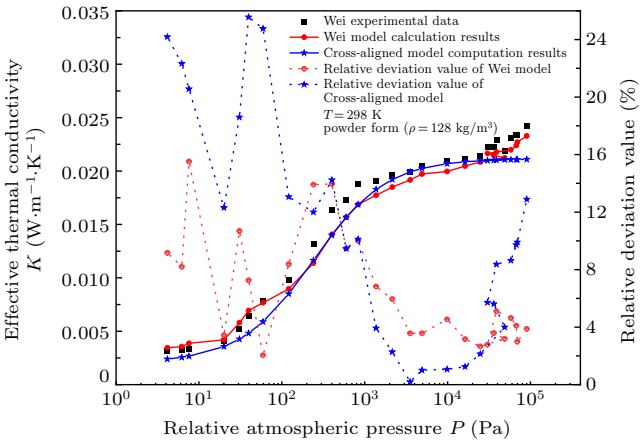


Fig. 9. Comparative validation of the variation of effective thermal conductivity of SiO_2 powdered aerogel with respect to changes in relative pressure.

As shown in Fig. 9, the calculated curves of the CACPM are consistent with the experimental data trend. Compared with the experimental data from Wei,[18] the structural model proposed by Wei[18] has a minimum deviation of 2.04% and an average deviation of 6.39%; while the CACPM results compared with the experimental data from Wei[18] have a minimum deviation of 0.2% and an average deviation of 10.51%. The specific deviation values are a minimum deviation of 0.00045 W/(m·K) and an average deviation of 0.001236 W/(m·K). In the pressure range of 10^3–10^4 Pa, the deviation between the calculated values and the experimental

values in this study is within 4%, indicating that the calculation accuracy of our proposed formula is superior to the Wei model.[18]

Next, the calculation results of the CACPM will be compared with the experimental data in Shen,[19] Bisson,[20] and the results calculated by the Wei[18] structure model under the same conditions, as shown in Figs. 10 and 11.

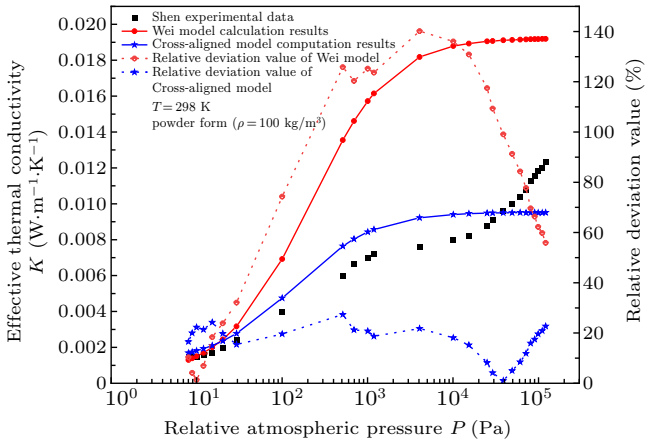


Fig. 10. Comparative validation of the variation of effective thermal conductivity of SiO_2 powdered aerogel with respect to changes in relative pressure.

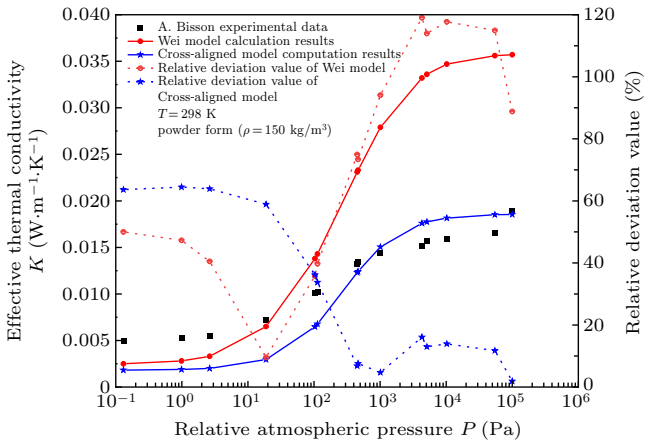


Fig. 11. Comparative validation of the variation of effective thermal conductivity of SiO_2 powdered aerogel with respect to changes in relative pressure.

In Fig. 10, within the pressure range of 10–10^4 Pa, the calculated results of the CACPM are basically consistent with the experimental data of Shen,[19] but show different trends within the range of 10^4–10^5 Pa. In comparison, the minimum deviation between the calculation results of the Wei[18] model and the experimental data of Shen[19] is 6.91%, with an average deviation of 75.64%. Meanwhile, the minimum deviation between the simulation results of the CACPM and Shen's[19] experimental data is 1.04%, with an average deviation of 16.84%. In Fig. 11, the minimum deviation between the calculation results of the Wei[18] structural model and the experimental data of Bisson[20] is 9.57%, with an average deviation of 72.85%. Whereas, the minimum deviation between the calculation results of the CACPM and Bisson's[20] experimental data is 6.81%, with an average deviation of 28.56%. Overall, under these two conditions, the calculation accuracy of the CACPM is superior to the Wei[18] model.

Then, the model is validated by comparing it with the experimental data of the effective thermal conductivity of particulate SiO_2 aerogels under different densities with changes in pressure. The results are also compared with Wei's[18] structure model under the same conditions. The relevant calculation parameters are set according to Wei[18] as follows: temperature $T = 298$ K, $a_2 = 0.85$,and the spherical macro-pore diameter in the particulate SiO_2 aerogel $D_1 = 3$ mm.

In Fig. 12, the minimum deviation between the calculation results of Wei's[18] model and the experimental data of Huang[21] is 0.16%, with an average deviation of 29.63%. The minimum deviation between the calculation results of the CACPM and Huang's[21] experimental data is 2.05%, with an average deviation of 33.82%. Within the pressure range of 10–10^3 Pa, the CACPM outperforms the Wei[18] model in prediction. However, within the pressure range of 10^3–10^8 Pa, the prediction performance of the CACPM is inferior to the Wei model.[18]

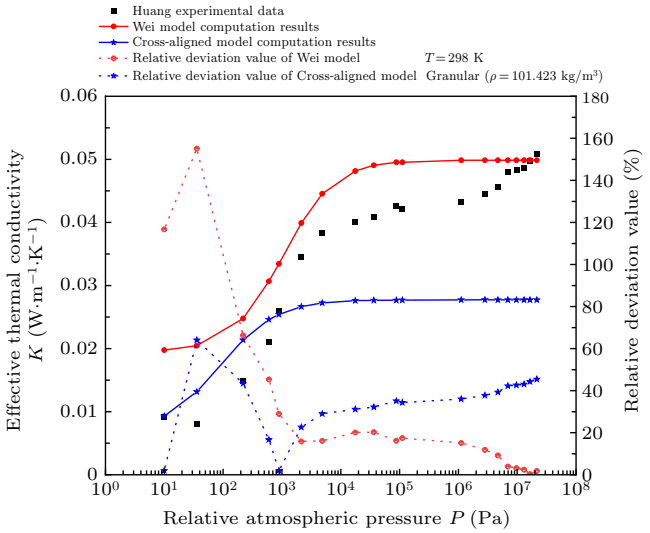


Fig. 12. Comparative validation of the variation of effective thermal conductivity of granular SiO_2 aerogel with respect to changes in relative pressure.

In Fig. 13, the minimum deviation between the calculated results of the Wei model[18] and the experimental data of Huang[21] is 3.82%, with an average deviation of 33.72%. With regard to the cross-aligned and cubic pore model, the minimum deviation compared to Huang[21] experimental data is 19.32%, with an average deviation of 42.39%. When the pressure exceeds 3×10^3 Pa, the calculation deviations of both models significantly increase.

In Fig. 14, the calculated results of the two models exhibit a similar changing pattern to the experimental data. The minimum deviation between the calculation results of the Wei model[18] and the experimental data from Wang[22] is 4.86%,

with an average deviation of 29.95%. With regard to the bimodal porous columnar structure model, the minimum deviation between the calculation results and the experimental data from Wang[22] is 13.28%, with an average deviation of 37.44%. When predicting the effective thermal conductivity of aerogel, the bimodal porous columnar structure model outperforms the Wei model[18] when the pressure is between 10^2–10^5 Pa. However, when the pressure is between 10–10^2 Pa, the bimodal porous columnar structure model is inferior to the Wei model.[18]

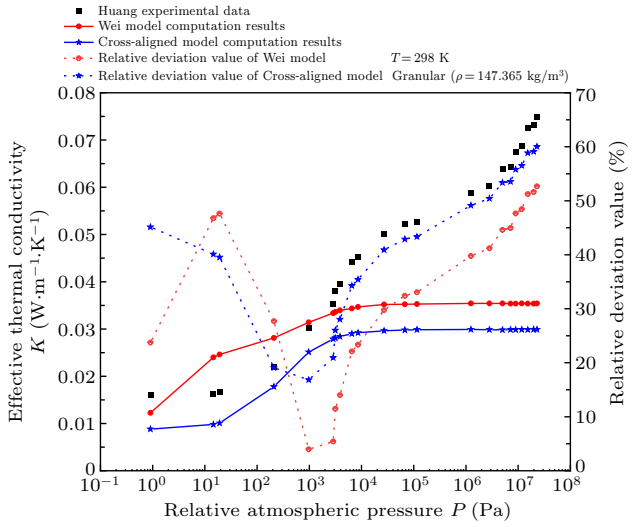


Fig. 13. Comparative validation of the variation of effective thermal conductivity of granular SiO_2 aerogel with respect to changes in relative pressure.

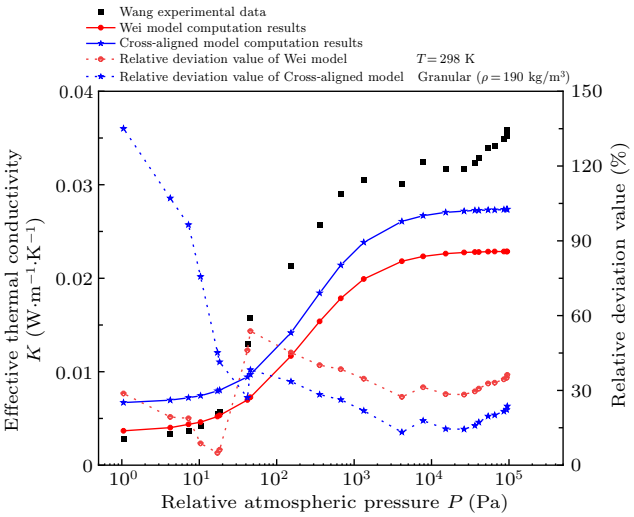


Fig. 14. Comparative validation of the variation of effective thermal conductivity of granular SiO_2 aerogel with respect to changes in relative pressure.

In conclusion, based on the analysis of the above data, our research model demonstrates a deviation of within 4% between calculated and experimental values for the thermal conductivity of powdery silica aerogel at a density of 128 kg/m^3 within the pressure range of 10^3–10^4 Pa. For the calculation of thermal conductivity of powdery silica aerogel at other densities, our research model consistently outperforms the Wei model.[18] With regard to the calculation of thermal conductivity of granular silica aerogel, both models exhibit some significant deviations, but they also yield results with relatively high accuracy within certain ranges.

5. Conclusion

(1) The cross-aligned and cubic pore model (CACPM) and heat transfer model were established based on the actual pore structure characteristics of aerogels: macroscopically, the model consists of large pores in the form of a cross-grid structure, while microscopically, it is composed of a cubic array of nanoballs. Heat transfer takes into account solid-phase conduction, gas-phase conduction, and radiative heat transfer.

(2) Based on the CACPM, the formula for calculation of the effective thermal conductivity of aerogels was derived using the thermodynamic principles of heat transfer:

$$k = k_{\mathrm{e}} + k_{\mathrm{r}} = \frac{\pi\delta k_{\mathrm{n}}}{\mu^2}\left(\mu + \frac{2}{\delta}\ln\frac{2}{\mu\delta+2}\right) + k_{\mathrm{n}}\left(1 - \frac{\pi\delta^2}{4}\right) + \frac{16n^2\sigma}{3\rho\sigma_{\mathrm{e,R}}}T^3.$$

(3) In this study, for powdery silica aerogel with a density of 128 kg/m^3 under the conditions of temperature at 298 K and pressure within the range of 0–10^5 Pa, the average deviation between the calculated thermal conductivity values and experimental values is 10.51%, with a minimum deviation of 0.2%. Within the pressure range of 10^3–10^4 Pa, the deviation between the calculated and experimental values is within 4%. Under other density conditions, the deviation between the model's calculated results and experimental values is significantly lower than that of the Wei model. However, both models exhibit relatively large deviations when calculating the effective thermal conductivity of granular silica aerogels, although they also have ranges of high precision. Overall, this model demonstrates higher applicability to the calculation of the thermal conductivity of powdery silica aerogel compared to the Wei model.

(4) In the calculation of the effective thermal conductivity of powdery silica aerogels, the significant errors attributed to different densities suggest that the values of parameters a_2 and D_1 may need to be correlated with density. For the calculation of the effective thermal conductivity of granular silica aerogels, new models and derivation methods might be necessary.

Acknowledgements

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