

Study on Thermal Conductivity of Gas Phase in Nano-porous Aerogel

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Abstract Nano-porous aerogel has an ultra low thermal conductivity and is usually used as the super insulator. To evaluate the insulation performance of the aerogel, we focus on studying the thermal conductivity of gas phase in the aerogel. We present a modified model to take into account the effect of non-uniform pore-size distribution on the gaseous thermal conductivity, and the present model predicts more agreement results with available data than the existing models. The gaseous thermal conductivity of the aerogel at high temperature gradient condition is also numerically studied. We also study the effect of the thermal transpiration flow on the gaseous thermal conductivity, and the results shows that the thermal transpiration flow effect leads to a reduction of the gaseous thermal conductivity.

Keywords: Thermal conductivity, Nano-porous aerogel, Gas phase, Thermal transpiration

1. Introduction

Nano-porous aerogel is a type of material with high specific surface area, high porosity, low density, low thermal conductivity and ultra low dielectric constant, which is of great potentials to be used in many fields including chemistry, aerospace, electronics, and acoustic or thermal insulation [1-3]. The total effective thermal conductivity of the aerogel can even be lower than that of the free air at room temperature, and thus the aerogel has been directly used as thermal insulation materials especially in extreme conditions [4-7]. It has been shown that the gas thermal conductivity in the aerogel has significant contribution to the total thermal conductivity under normal ambient conditions.

In addition to the gas species and gas pressure in the aerogel, pore-size also has great impact on the gaseous thermal conductivity, and thus the theoretical models of the gaseous thermal conductivity are usually established based on the gas species, gas pressure and pore-size. However, in the most existing models, the average pore size is employed when calculating the gas thermal conductivity, which will inevitably bring significant computational errors because the pore-size in the real material usually has an extreme non-uniform and random distribution. For this

reason, a modified model with the consideration of the non-uniform and random distribution of the pore-size will be established to improve the prediction accuracy for the gaseous thermal conductivity. In addition, the effect of transpiration flow on the gas thermal conductivity has not been reported in the literature.

2. Molecular Dynamics Simulation for Gas Phase

In this section, we focus on studying the effect of the pore size on the thermal conductivity of the gas phase in the nano-pores of the aerogel.

2.1 Numerical model

The Molecular Dynamics (MD) method is employed to study the energy transfer between the gas molecules for prediction of the gaseous thermal conductivity. We establish two types of pores, i.e. open pore and close pore as shown in Fig. 1. The close pore denotes that the gas molecules are enclosed in the pore, and the gas molecules do not exchange heat and mass with the external environment, while the open pore denotes that the gas molecules exchange mass and energy with the environment.

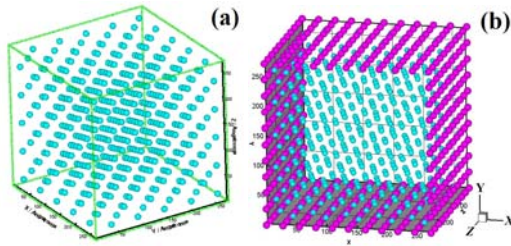


Fig.1 Modeling of the molecular in nano-pores.
 (a) Close pore. (b) Open pore

The simulated fluid is the nitrogen gas for the gaseous thermal conduction. We assume that the nitrogen is LJ fluid, i.e. the molecular force obeys the Lennard-Jones potential function $U(r_{ij}) = 4\epsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6]$, where ϵ is the maximum potential depth corresponding to the energy, σ is the length scale parameter, r_{ij} is the inter-particle separation, and i and j denote the particles i and j , respectively. For nitrogen molecule, $\sigma = 3.32 \text{ \AA}$, $\epsilon/k_B = 37.2 \text{ K}$ [8]. In the simulations, the canonical ensemble (NVT) is used for the statistics of the molecular information. The gaseous thermal conductivity is calculated by the Green-Kubo relation. [9]. The time step is set 2fs, and the simulation runs 500000 steps. The initial conditions are (1) FCC structure for the molecules and (2) molecular velocities obey the Gauss distribution. The boundary conditions include diffuse boundary and periodic boundary. For the close pore, all the boundaries of the simulation cell (box) are the diffuse boundary, i.e. when the molecules collide with the boundary, they are reflected back diffusively. For the open pore, the periodic boundary is set in the z -direction, and other boundaries of the box are also set to be the diffuse boundary. The pore size is defined as the side length of the simulation cell, which ranges from 16.37 to 70.09nm for the close pore with molecule number from 108 to 8788, and from 16.37 to 87.29nm for the open pore with molecule number from 108 to 16384.

2.2 Results

Figure 2 shows the effect of the pore size on the gaseous thermal conductivity in the nano-pore.

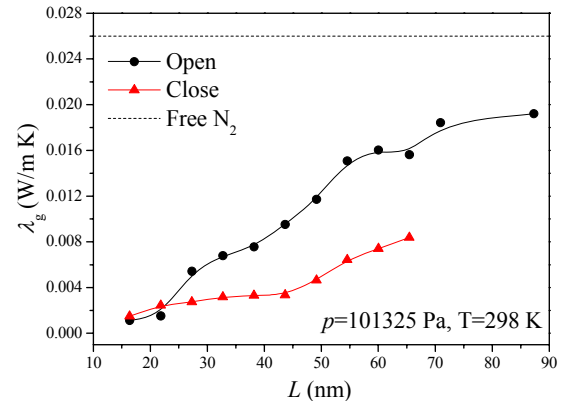


Fig. 2 Effect of the pore size on the gaseous thermal conductivity in nanoscale pores

For the close pore, we can see that the gaseous thermal conductivity increases with the increase of the pore size, and the gaseous thermal conductivity will increase more significantly when the pore size is over around 40 nm, but the thermal conductivity is still much less than that of the free nitrogen. This can be attributed to two factors: (1) the pore boundaries can limit the mean free path of the gas molecules, resulting in a reduction of the heat transfer, and (2) the diffuse boundaries enclose the gas molecules in the pore and isolate the gas from the environment, which significantly suppress the heat conduction via the gas molecules. For the open pore, we can see that the gaseous thermal conductivity also increases as the pore size becomes large. However, because the gas molecules can exchange the energy and mass with the external environment, the thermal conductivity in the open pores is much higher than that in the close pores. Due to the existence of the diffuse boundaries in the x - and y -directions, the mean free path of the gas molecules is also suppressed. Therefore, the thermal conductivity is still lower than that of the free gas. Compared with the close pore, we can find that the gaseous thermal conductivity in the open pores is about one time higher than that in the close pores.

2.3 Effect of non uniform pore-size distribution on gaseous thermal conductivity

The pore size in aerogel usually presents a random and non-uniform distribution, see Fig. 3. Since the gaseous thermal conductivity

strongly depends on the pore size, in this section we will discuss how the non-uniform distributed pores affect the gaseous thermal conductivity.

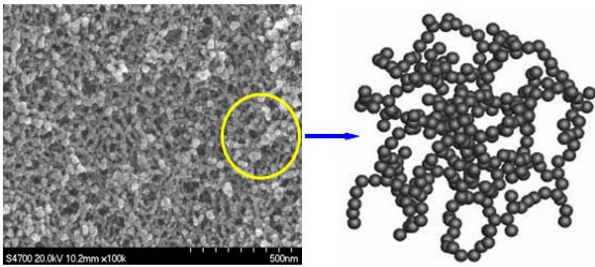


Fig. 3 Pore size structure in aerogel

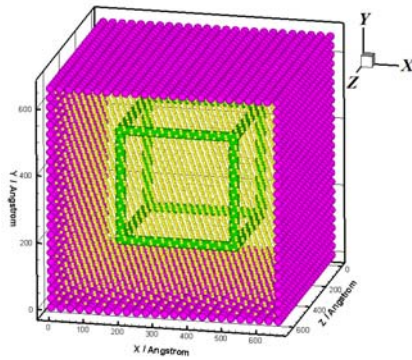


Fig. 4 Pore structure with two pore sizes

Figure 4 shows the structure employed to simulate the gas molecules in different pores, where the small green cubic backbone (solid phase) denotes the small pore enclosed in the large pore, and the periodic boundary is used in the z-direction of the large pore. The molecular force between the gas molecules and the solid phase is assumed to obey the LJ function, and the parameter of nitrogen is used for the approximation of the solid phase.

From Fig. 5(a), we can observe that the small pore has little effect on the gaseous thermal conductivity compared with the large pore, while the large pore dominate the gaseous thermal conductivity. In addition, from Fig. 5(b), the gaseous thermal conductivity in the structure with different pore size is lower than that in the single pore, and the reason can be attributed to the solid backbone of the small pore, which can attract gas molecules and reduce the mean free path of gas molecules.

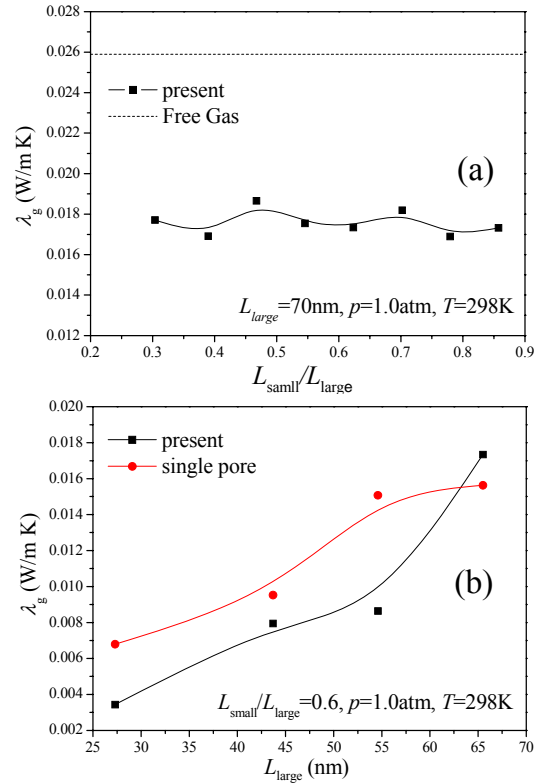


Fig. 5 Gaseous thermal conductivity in the structure with different pore sizes. (a) Effect of the small pore. (b) Effect of the large pore

The structure in Fig. 6 is employed to simulate the gas molecules in non-uniform pores, where the two intersected green solid backbones are composed of nano-particles, and the location of the intersection can reflect the non-uniformity of the pore size distribution, i.e. the intersection location closer to the centre of the structure means a more uniform pore size distribution is. Therefore, we can focus on the effect of the location of the intersection on the gaseous thermal conductivity, and the results are shown in Fig. 7.

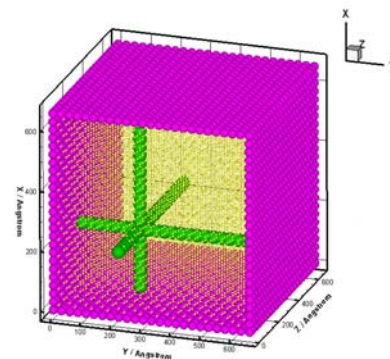


Fig. 6 Modeling of the structure with the non-uniformly distributed pore size

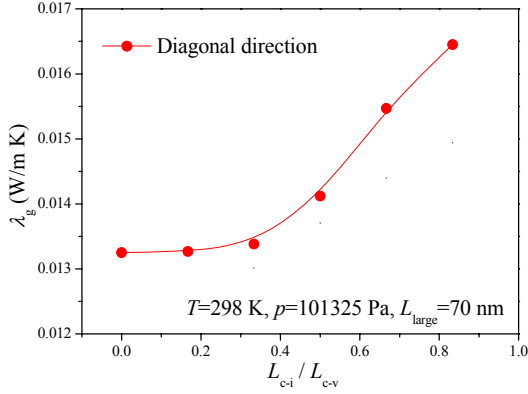


Fig. 7 Effect of non-uniformity of pore size distribution on gaseous thermal conductivity

In this study, we use a non-dimensional parameter L_{c-i}/L_{c-v} to reflect the non-uniformity of the pore size distribution, and a smaller value of L_{c-i}/L_{c-v} denotes the more uniformity of the pore size distribution, and vice versa. L_{c-v} denotes the distance between the pore centre and the cubic vertex, and L_{c-i} denotes the distance between the pore centre and the intersection point of the two backbones. The intersection point changes along the direction of the cubic diagonal.

From Fig. 7, we can see that the gaseous thermal conductivity increases with the increase of L_{c-i}/L_{c-v} , which denotes that the non-uniformity of the pore size distribution can increase the gaseous thermal conductivity in nano-porous media. Therefore, to predict the gaseous thermal conductivity for aerogels accurately, it is necessary to consider the effect of pore size distribution.

3. Theoretical Model for Gas Phase

3.1 Theoretical model

The widely used model of the gaseous thermal conductivity in porous media is Kaganer's model, given by [10]:

$$\lambda_g = \lambda_g^0 / (1 + 2\beta Kn) \quad (1)$$

where λ_g^0 is the thermal conductivity of the gas in free space, β is a coefficient depending on the accommodation coefficient and the adiabatic coefficient of the gas, and Kn is the Knudsen number defined as the ratio of the mean free path l_g of the gas molecules to the mean pore diameter D of the porous media. The mean free path l_g can be calculated by the following equation:

$$l_g = k_B T / \sqrt{2} \pi d_g^2 p_g \quad (2)$$

where d_g is the diameter of the gas molecule, n_g is the number density of gas molecule, k_B is the Boltzmann constant, T is the gas temperature, and p_g is the gas pressure

Zeng et al. [11] developed an analytical solution based on the gas kinetics for the gaseous thermal conductivity:

$$\lambda_g = \frac{(2.25\gamma - 1.25)0.461(p_g / k_B T)C}{0.25S\rho_a / \Phi + \sqrt{2}(p_g / k_B T)\pi d_g^2} \quad (3)$$

where, $C = (8k_B T / m_g \pi)^{0.5} c_V / N_A$, γ is the adiabatic coefficient of the gas, m_g is the mass of the gas molecule, N_A is the Avogadro's constant, c_V is the constant volume heat capacity, ρ_a is the density of the aerogel, Φ is the porosity, and S is the specific surface area..

Equations (1) and (3) are currently the most popular theoretical models for the gaseous thermal conductivity, and in this paper we refer to them as Kaganer's Model and Zeng's Model, respectively. Due to the simplicity and convenience, we prefer to use of Kaganer's model for the predictions.

The pore size in the material usually distributes non-uniformly and randomly. To obtain accurate predictions, Reichenauer *et al.* [12] assumed that the pore size in aerogel obeys the Gauss distribution, and the total gaseous thermal conductivity is the sum of the gaseous thermal conductivity in each pore, given by:

$$\lambda_g = \frac{1}{N} \int \frac{\lambda_g^0}{1 + 2\beta l_g / D'} e^{-\frac{(D'-D)^2}{2\sigma^2}} dD' \quad (4)$$

where D' is the convolution variable, σ is the standard deviation in the Gauss distribution function, of which the physical meaning is the distribution width of the pore size, and N is a factor that normalizes the integration to provide the correct total porosity. Usually, we make the pore size distribute in the confidence interval $[D - 3\sigma, D + 3\sigma]$ to make sure that the total proportion of the pore-size distribution is close to 1.0, expressed as:

$$\int_{D-3\sigma}^{D+3\sigma} \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{(D'-D)^2}{2\sigma^2}} dD' \approx 0.9974 \quad (5)$$

The Gauss model of Eq. (4) includes an assumption, i.e. the pore size obeys the Gauss distribution, which is a symmetry distribution, but in the real aerogel, the pore size distribution usually is not symmetry but a non-uniform distribution, see Fig. 8.

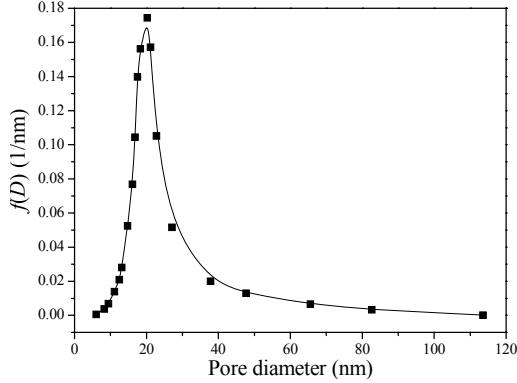


Fig.8. Pore size distribution of silica aerogel [13]

Figure 8 shows the measured data of the pore size distribution from silica aerogel, and we can clearly find that the distribution range of the large pores is wider than that of the small pores with respect to the mean pore diameter. Figure 8 suggests that the Gauss distribution function cannot yet accurately predict the pore size distribution in aerogel. The large pores have more contribution to the gaseous thermal conductivity, just as shown from the MD simulations. For this reason, we assume the pore-size distribution function as the following form:

$$\Phi_i = \begin{cases} 0 & D_i \in [D-3\sigma, D-\sigma] \\ \frac{\Delta D}{\sqrt{2\pi\sigma}} e^{-\frac{(D_i-D)^2}{2\sigma^2}} & D_i \in [D-\sigma, D+\sigma] \\ \frac{2\Delta D}{\sqrt{2\pi\sigma}} e^{-\frac{(D_i-D)^2}{2\sigma^2}} & D_i \in (D+\sigma, D+3\sigma] \end{cases} \quad (6)$$

where, i is the pore index. We assume that the pore size still obeys the Gauss distribution in the confidence interval $[D-\sigma, D+\sigma]$, and thus we can guarantee that 68.26 percent of the pores obey the Gauss distribution. Once in the interval of $[D+\sigma, D+3\sigma]$, the value of the probability function will be doubled based on the original value of the Gauss distribution function. According to the above assumptions, the total probability of the pore size

distribution by integrating Eq. (6) also meets 99.74 percent. We also assume that all the pores of different sizes in the porous material act as parallel paths, and then the total gaseous thermal conductivity also can be written as a superposition form:

$$\lambda_g = \sum_{i=1}^n \Phi_i K(D_i) \quad (7)$$

where, n is the number of the pores $K(D_i)$ is a simplified form of Eq. (1) with respect to the pore size D_i . We refer to Eqs. (6) and (7) as the present modified model.

3.2 Validation of the present model

In this section, we use three types of aerogels, and the gaseous thermal conductivity of these materials will be examined by the present model, Zeng' Model, Kaganer's Model and Gauss model, respectively, together compared with available experimental data.

In Refs. [11, 13], the sample of the silica aerogel is filled with air at room temperature, and the mean pore diameter of the aerogel is $D = 20$ nm. But we assume that the distribution of the pore size obeys the statistical laws, so the pore-size samples have a mathematical expectation of $D = 29.12$ nm and a standard deviation of $\sigma = 28.03$ nm.

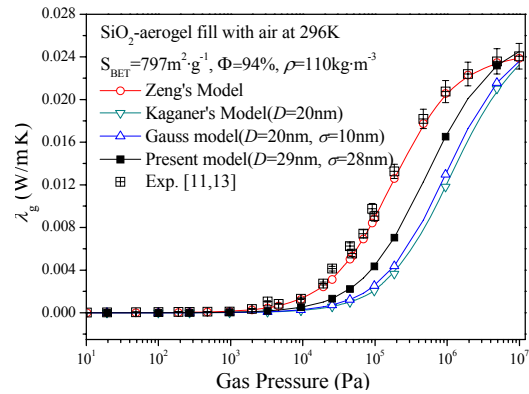


Fig. 9 Pressure dependence of gaseous thermal conductivity in silica aerogel

Figure 9 shows the results calculated by different models. We can see that the predictions calculated by Kaganer's Model and Gauss model are not in good agreement with the experimental data while the present model improves the prediction accuracy significantly. In addition, the results from Zeng's Model have the best agreement with

the experimental data. Maybe we can infer that for the silica aerogel, Zeng's Model presents good performance to predict the gaseous thermal conductivity.

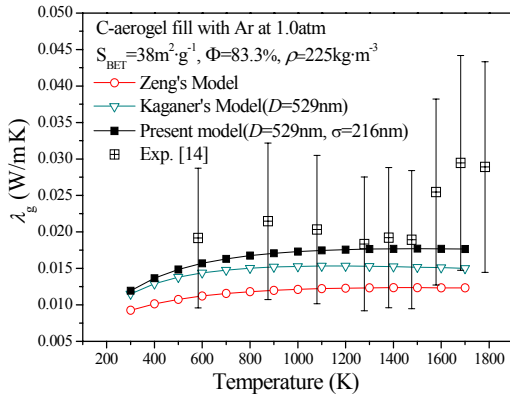


Fig. 10 Gaseous thermal conductivity in carbon aerogel at different temperatures

The second tested sample is the carbon aerogel in Ref. [14]. The measured mean pore diameter is $D = 529$ nm with a measurement error of 106nm, and thus we can assume that the primary distribution width of the pore size is $\sigma = 2 \times 106$ nm. The compared results are shown in Fig. 10, and we can easily find that the present model is of the best performance among all the models.

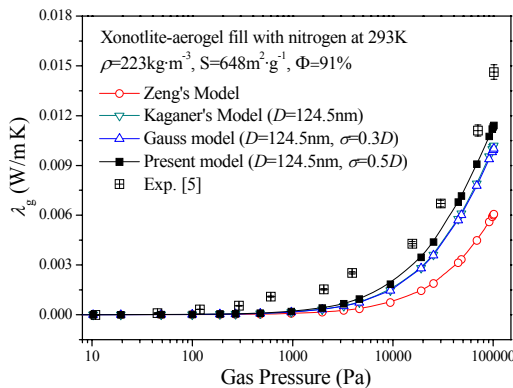


Fig. 11 Pressure dependence of gaseous thermal conductivities in xonotlite-aerogel

The present model is also tested by the xonotlite-aerogel in Ref. [5]. The mean pore diameter is derived from the density. According to Ref. [15], the mean pore diameter of those aerogels with non-uniform pores can be estimated by $D \approx (3\pi^2 / 16\rho_p d_p) / \rho_a$, where d_p is the solid particle size, and for the xonotlite-aerogel we can use $d_p \approx 6$ nm according to Ref. [5]. From Fig. 11, we can find that the present model

also has the highest accuracy. The deviations between the predictions and measured data probably can be attributed to the coupling effect. From the above analysis, we can find that the present model can significantly improve the prediction accuracy for the gaseous thermal conductivity.

4. Effect of thermal transpiration flow on the gaseous thermal conductivity

Aerogel is often used as thermal insulation material especially in extreme thermal conditions, in which a large temperature gradient occurs in the material. Once the gas is confined in the nano- or micro-scale pores, the wall temperature gradient can propel gas molecules to flow from cold side to hot side, i.e. thermal transpiration flow [16], and then the gas flow will affect the gas conduction in the nano-porous aerogel significantly. In this study, a R26 moment method [17-18] is employed to investigate the effect of thermal transpiration flow on the effective thermal conductivity of non-equilibrium argon gas. This method is an extended thermodynamic method to simulate the non-equilibrium phenomenon of gas flow by solving the Boltzmann equation approximately.

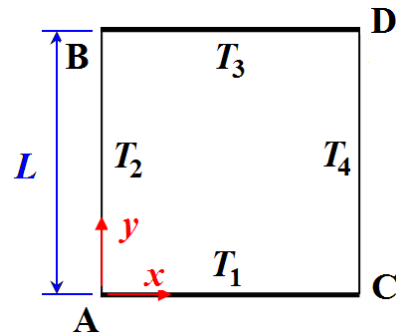


Fig. 12 Schematic of the simulation domain

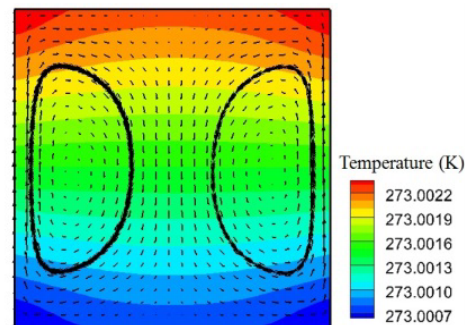


Fig. 13 Temperature distribution and velocity vectors of the gas in the simulation domain

As schematic in Fig. 12, we calculate the effective thermal conductivity of argon gas confined between two parallel plates (AC and BD) while the other two boundaries (AB and CD) are treated as symmetry boundary condition. The ambient pressure is kept at 101325 Pa. We change the distance (L) of the two plates from 100 nm to 250 nm, for different Knudsen numbers while the temperature gradient is fixed at 3.0×10^4 K/m. To study the thermal transpiration flow, the boundaries (AB and CD) are regarded as wall boundaries with a linear temperature distribution. On this condition, the gas is propelled by the wall temperature gradient and forms a thermal transpiration flow, as shown in Fig. 13. First, the gas near the AB and CD walls flows from the cold to the hot, and simultaneously the pressure gradient also drives the gas from the hot to cold in the middle region, and thus a circular flow appears between the two plates. This circular flow will inevitably affect the gas thermal conduction, and the gaseous thermal conductivity must be different from that predicted by the classical relations which are established on the static gas.

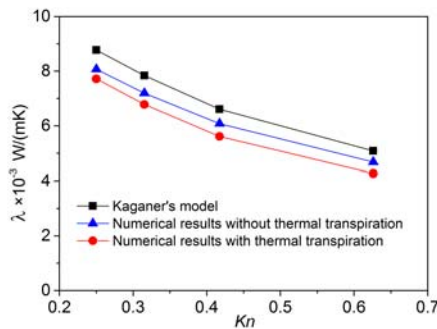


Fig. 14 The effective thermal conductivity under different Knudsen numbers

The predicted thermal conductivity under the two conditions with and without considering the thermal transpiration effect is compared with Kaganer's Model in Fig. 14. As we can see, the thermal conductivity with the thermal transpiration flow effect is lower than that of the other cases. This is because part of the heat flux is consumed by the flow resistance of thermal transpiration flow. The effect of thermal transpiration flow on the thermal conductivity of non-equilibrium gas in nano- or micro-scale pores is under way in the

authors' group.

5. Conclusions

The Molecular Dynamics method is employed to study the gas energy transport in the nano-pores. The pore size distribution affects the gaseous thermal conductivity of the nano-porous media significantly, and a more non-uniform pore size distribution usually leads to a higher gaseous thermal conductivity. To improve the prediction accuracy of the theoretical model for the gaseous thermal conductivity, we introduce the random and non-uniform pore size distribution function to modify the classical model, and the present model is proved to have higher prediction accuracy than the existing models. The thermal transpiration flow has been found to have important effect on the gaseous thermal conductivity of the non-equilibrium gas in the nanoscale pores, and the thermal transpiration flow reduces the gaseous thermal conductivity compared with the static gas phase.

Acknowledgment

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