



Prediction of the gaseous thermal conductivity in aerogels with non-uniform pore-size distribution

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ABSTRACT

The gaseous thermal conductivity in nano-porous aerogel is an important contribution to the total thermal conductivity under normal temperature and pressure condition. Pore-size distribution in the aerogel has significant effect on the gaseous thermal conductivity. The pore-size in the porous materials generally presents random and non-uniform distribution, and large deviation will be caused if directly using the mean pore-size to calculate the gaseous thermal conductivity. We present a modified model based on the previous theoretical models to take into account the random and non-uniform pore-size distribution, and the predicted results from the present model are significantly better than those of existing models.

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1. Introduction

Nano-porous aerogel is a potential kind of material with high specific surface area, high porosity, low density, low thermal conductivity and ultra low dielectric constant, which can be used in many science and technology fields, such as, chemistry, aerospace, electronics, and acoustic or thermal insulation [1–3]. In most cases, the total effective thermal conductivity of the aerogel is less than that of the free air at room temperature, and thus many aerogels have been directly used as thermal insulation materials especially in extreme conditions [4–8]. In the researches [9–12], we can find that gaseous 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.

The gaseous thermal conductivity λ_g as a function of the pore-size and gas pressure can be described as [13]:

$$\lambda_g = \frac{\lambda_g^0}{1 + 2\beta Kn} \quad (1)$$

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 as the following equation:

$$l_g = \frac{1}{\sqrt{2}n_g d_g} = \frac{k_B T}{\sqrt{2}n_g d_g p_g} \quad (2)$$

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 in the porous media. However, Zeng et al. [14,15] pointed out that l_g in Eq. (2) is the mean free path of the free gas instead of the mean free path of the real gas in the porous media, which leads to computational deviation when predicting the gaseous thermal conductivity. Therefore, they developed an analytical solution based on the gas kinetics for the gaseous thermal conductivity:

$$\lambda_g = \frac{(2.25\gamma - 1.25)0.461 (p_g/k_B T) (8k_B T/m_g \pi)^{0.5} c_V}{0.25S\rho_a/\Phi + \sqrt{2}(p_g/k_B T)\pi d_g^2} \frac{c_V}{N_A} \quad (3)$$

where γ is the adiabatic coefficient of the gas, m_g is the mass of the gas molecular, 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. Both Φ and S can be calculated from the pore size and the solid particle diameter of the aerogel [16].

Eqs. (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. From Refs. [14,15], we know that Zeng's Model is based on a rigorous theoretical system, but there is a lack of enough experimental data to verify it and the measurement of c_V in Eq. (3) is difficult under complex

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atmosphere conditions, which limit the convenience of Zeng's Model. Kaganer's Model has a simple form and calculation convenience, so that in this study we prefer to Kaganer's mode for the prediction of the gaseous thermal conductivity.

Note that the parameter D with respect to Kn in Eq. (1) is the mean pore diameter of the porous media, but in practice, the pore-size in the material usually has an extreme non-uniform and random distribution, and using the mean pore diameter D to calculate the gaseous thermal conductivity will inevitably bring significant computational errors. For this reason, the purpose of this study is to establish a modified model with the consideration of the non-uniform and random distribution of the pore-size, and improve the prediction accuracy for the gaseous thermal conductivity.

2. Theoretical models

In order to approximately describe the non-uniform distribution of the pore-size, Reichenauer et al. [17] assumed two different mean pore-sizes (D_1, D_2) and two contributions (Φ_1, Φ_2) to the total porosity with respect to the large and small pores in the porous media, and the thermal conduction acts as parallel paths in different pores, and then the total gaseous thermal conductivity can be written as a superposition form:

$$\lambda_g = \frac{\lambda_g^0 \Phi_1}{1 + 2\beta l_g / D_1} + \frac{\lambda_g^0 \Phi_2}{1 + 2\beta l_g / D_2} \tag{4}$$

Moreover, to consider the random distribution of the pore-size, Reichenauer et al. [17] chose the Gauss distribution function to approximate the pore-size distribution, and the total gaseous thermal conductivity is the sum of the gaseous thermal conductivity in each pore:

$$\lambda_g = \frac{1}{N} \int \frac{\lambda_g^0}{1 + 2\beta l_g / D'} \cdot e^{-\frac{(D'-D)^2}{2\sigma^2}} dD' \quad D' > 0 \tag{5}$$

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.

Eq. (5) seems to be a good formula to predict the gaseous thermal conductivity, but it is not convenient in application, because the factor N must be separately calculated. To improve the computational convenience, and inspired by the ideas in Eqs. (4) and (5), we 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:

$$\lambda_g = \sum_{i=1}^n \Phi_i K(D_i) \tag{6}$$

where n is the number of the pores, i is the pore index, Φ_i is the contribution to the total porosity and $K(D_i)$ is a simplified form of Eq. (1) with respect to the pore-size D_i . Here, we still use the Gauss distribution function to approximately calculate Φ_i , yielding:

$$\Phi_i = \int_{D_i}^{D_i+\Delta D} \frac{1}{\sqrt{2\pi\sigma}} e^{-\frac{(D'-D)^2}{2\sigma^2}} dD' \approx \frac{\Delta D}{\sqrt{2\pi\sigma}} e^{-\frac{(D_i-D)^2}{2\sigma^2}} \quad (D_i > 0) \tag{7}$$

We can see from Eq. (7) that Φ_i can be understood as the probability when the pore-size D' is in the size interval of $[D_i, D_i + \Delta D]$. If n is large enough, we can obtain the total gaseous thermal conductivity:

$$\lambda_g \approx \sum_{i=1}^n \left[\frac{\Delta D}{\sqrt{2\pi\sigma}} e^{-\frac{(D_i-D)^2}{2\sigma^2}} \right] \cdot K(D_i) \quad (D_i > 0) \tag{8}$$

According to the Gauss distribution function, as the pore-size distributes in the confidence interval $[D - 3\sigma, D + 3\sigma]$, the total proportion of the pore-size distribution is:

$$\lim_{n \rightarrow \infty} \sum_{i=1}^n \Phi_i = \int_{D-3\sigma}^{D+3\sigma} \frac{1}{\sqrt{2\pi\sigma}} e^{-\frac{(D'-D)^2}{2\sigma^2}} dD' \approx 0.9974 \quad (D-3\sigma > 0) \tag{9}$$

We can ignore the contributions to the total porosity of those pore-sizes which are not in the confidence interval $[D - 3\sigma, D + 3\sigma]$. From the above analysis, we can completely use Eqs. (6) and (7) to replace Eq. (5), and in this paper we refer to Eqs. (6) and (7) as Gauss model.

However, if using Eqs. (6) and (7) or Eq. (5) to calculate the gaseous thermal conductivity in the porous media, the calculation errors still will be brought in, and the results compared with the experimental data will be shown in the next section, and here we only analyze the reasons of the caused errors. Firstly, the local pore-sizes such as $D_i = D + \xi$ and $D_i = D - \xi$ have the same contributions to the total porosity of the material, i.e. they have an equal probability calculated by Eq. (7), but different contributions to the total gaseous thermal conductivity, because the large pores contribute much more to the gaseous thermal conductivity than the small pores. Secondly, Figs. 1 and 2 present the distribution of the pore size in some typical nano-porous aerogels [18,19], 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.

Therefore, Gauss distribution function is not able to completely describe the distribution of all the pore-sizes in the nano-porous media. Moreover, we should also enhance the contributions of the large pores to the total gaseous thermal conductivity, and simultaneously decrease the contributions of the small pores. Therefore, we assume the pore-size distribution function as the following form:

$$\Phi_i = \begin{cases} \frac{\Delta D}{\sqrt{2\pi\sigma}} e^{-\frac{(D_i-D)^2}{2\sigma^2}} & D_i \in [D-\sigma, D+\sigma] \quad D_i - \sigma > 0 \\ \frac{2\Delta D}{\sqrt{2\pi\sigma}} e^{-\frac{(D_i-D)^2}{2\sigma^2}} & D_i \in (D+\sigma, D+3\sigma] \end{cases} \tag{10}$$

Here, we change the confidence interval $[D - 3\sigma, D + 3\sigma]$ to $[D - \sigma, D + 3\sigma]$, and 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% 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

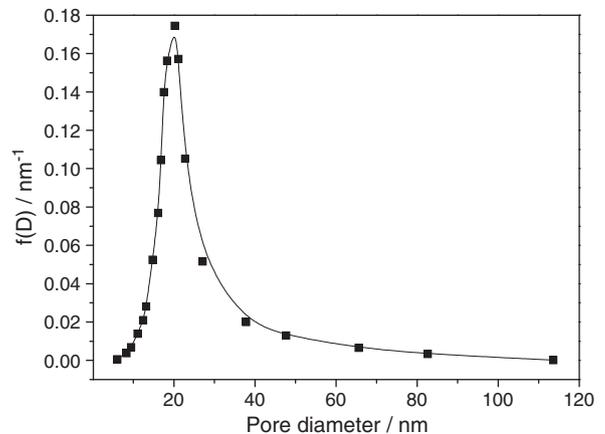


Fig. 1. Normalized pore size distribution of silica aerogel [18].

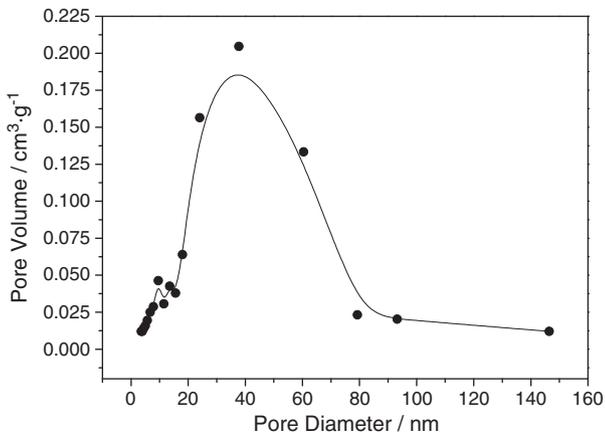


Fig. 2. Pore size distribution of polyisocyanurate aerogel by nitrogen adsorption [19].

to the above assumptions, the total probability of the pore size distribution by integrating Eq. (10) also meets 99.74%, but the contributions to the total gaseous thermal conductivity from the large pores are enhanced, and we refer to Eqs. (6) and (10) as the present modified model.

3. Validation of the present model

In this section, we use six types of aerogels from the previous literature, 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 the literature. In addition, Eqs. (11)–(13) can help us to calculate some necessary parameters which were not listed in the literature:

$$\Phi = 1 - \frac{\rho_a}{\rho_p} \quad (11)$$

$$D = \frac{4V_{pore}}{S_{ext}} \quad (12)$$

$$V_{pore} = \frac{1}{\rho_a} - \frac{1}{\rho_p} \quad (13)$$

where V_{pore} is the pore volume and ρ_p is the density of the skeletal particle.

In Refs. [18,14], the sample of the silica aerogel is filled with air at room temperature, and from Fig. 1 the obtained mean pore diameter of the aerogel is about $D=20$ nm. However, if we assume that the distribution of the pore-size obeys the statistical laws, the pore-size samples (symbols in Fig. 1) have a mathematical expectation of $D=29.12$ nm and a standard deviation of $\sigma=28.03$ nm. Fig. 3 shows the results calculated by different models detailed in Section 2. 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.

The second tested sample is the carbon aerogel in Ref. [20]. The measured mean pore diameter is $D=529$ nm with a measurement error of 106 nm, 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. 4, and we can easily find that the present model is of the best performance among all the models.

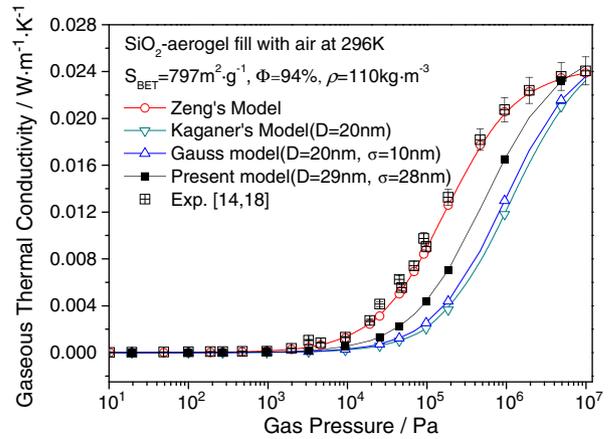


Fig. 3. Pressure dependence of gaseous thermal conductivity in silica aerogel.

Fig. 5 shows the calculation results for other nano-aerogel samples of silica aerogel and fumed aerogel in Ref. [17]. However, in Ref. [17], the measurement uncertainties of the mean pore diameters for these two aerogels were not given, so we assume that the distribution width of the pore size is $\sigma=0.5 \times D$. Firstly, for the silica aerogel, the measured mean pore diameter is $D=4 V/S_{ext}=73$ nm or $D_{SAXS}=65$ nm, which is obtained from nitrogen sorption via t-plot or small angle X-ray scattering data (SAXS), respectively. Because the measured values of D and D_{SAXS} are close, we can believe that the effective mean pore diameter is 73 nm. The results calculated by different models are shown in Fig. 5(a). If we fit the experimental data to the Kaganer's Model, the estimated mean pore diameter will be 100 nm which is much larger than 73 nm. Therefore, if directly substituting the measured mean pore diameter of 73 nm into the Kaganer's Model or Gauss model, we cannot acquire accurate results. However, the present model can significantly improve the prediction accuracy. In addition, note that Zeng's Model shows the best prediction accuracy in Fig. 3 for the silica aerogel while in this case the present model even predicts better than Zeng's Model.

Secondly, for the fumed aerogel, the measured mean pore diameter is $D=4 V/S_{ext}=100$ nm or $D_{SAXS}=115$ nm, and we can believe the effective mean pore diameter is 100 nm since the two values are quite close. From Fig. 5(b), we can find that all of the theoretical models in Section 2 are not able to accurately predict the gaseous thermal conductivity, but the results calculated by the present model approach the best to the experimental data. If we fit the experimental data to the

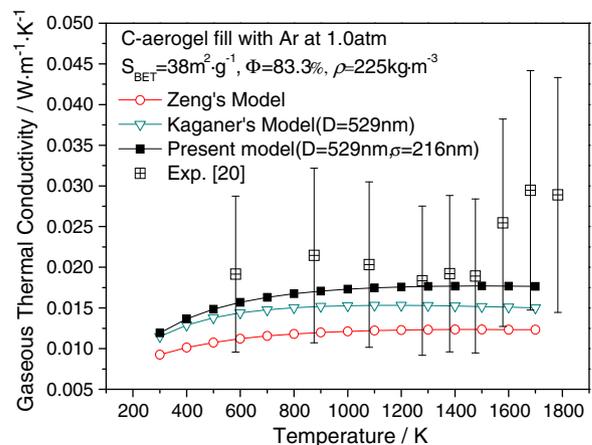


Fig. 4. Gaseous thermal conductivity in carbon aerogel at different temperatures.

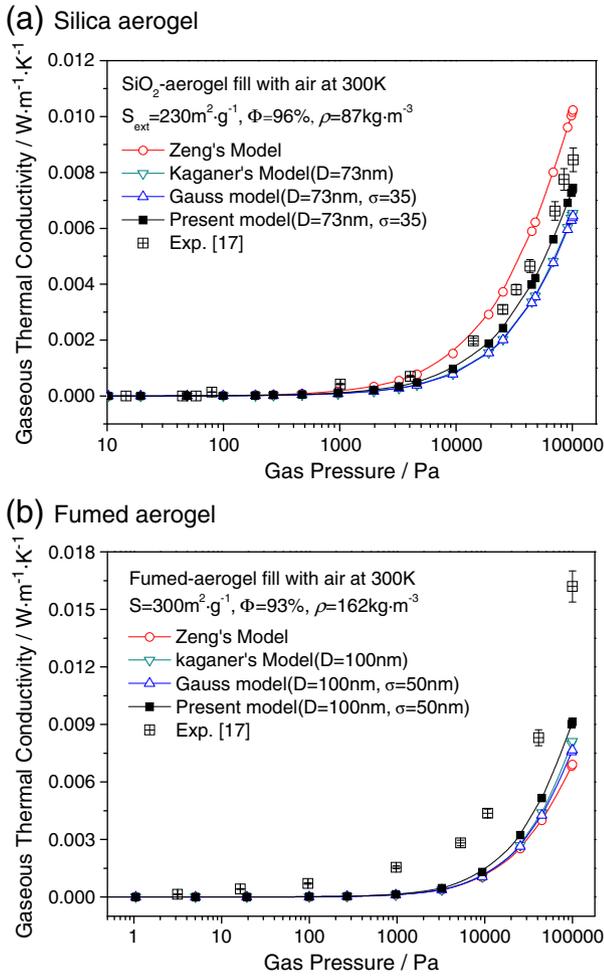


Fig. 5. Pressure dependence of gaseous thermal conductivities in aerogels.

Kaganer's Model, the estimated mean pore diameter will be 300 nm, which inevitably brings great errors, and the reasons of the errors were explained in Ref. [17], but another reason is probably originated from the coupling effect—an additional thermal conductivity resulted from the heat transfer via the interaction between the solid and gas in the aerogel.

The present model is also tested by the composite aerogel, and the tested sample is xonotlite–aerogel in Ref. [11]. However, only the density is available in the reference, so that the most important parameter—the mean pore diameter has to be derived from the density. According to Ref. [10], the mean pore diameter of those aerogels with non-uniform pores can be estimated by Eq. (14)

$$D \approx \left[\frac{3\pi^2}{16} \rho_p \cdot d_p \right] \rho_a^{-1} \quad (14)$$

where d_p is the solid particle size, and for the xonotlite–aerogel we can assume $d_p = 6$ nm according to Ref. [21]. In order to guarantee high porosities of the xonotlite–aerogels (>90%)[11], we assume $\rho_p = 2500$ kg/m³. Then, we can obtain the gaseous thermal conductivities of the xonotlite–aerogel, and the results are shown in Fig. 6. From Fig. 6, we can find that the present model does have the best performance to predict the gaseous thermal conductivity, but some deviations still exist between the predictions and experimental data, and one of the most important reasons is the coupling effect. Fig. 6 also reflects that the contribution to the total gaseous thermal conductivity via the coupling is of the same order of magnitude as

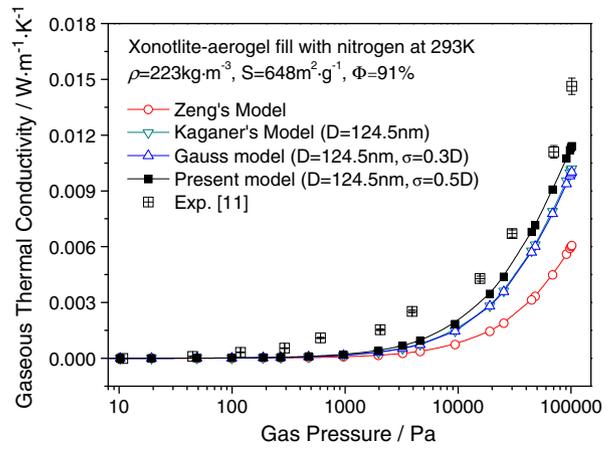


Fig. 6. Pressure dependence of gaseous thermal conductivities in xonotlite–aerogel.

that via the gas-phase transport, especially for the gas pressure between 100 Pa and 11,000 Pa.

The last sample is a type of organic aerogel with mean pore diameter 600 nm named resorcinol-formaldehyde-based aerogel (RF0.6) in Ref. [22] and the total effective thermal conductivity of the material is experimentally presented. From Fig. 7(a), we can find that the gaseous thermal conductivities calculated by the present model are significantly higher than those by the other models, because the present model can enhance the contributions of the large pores to

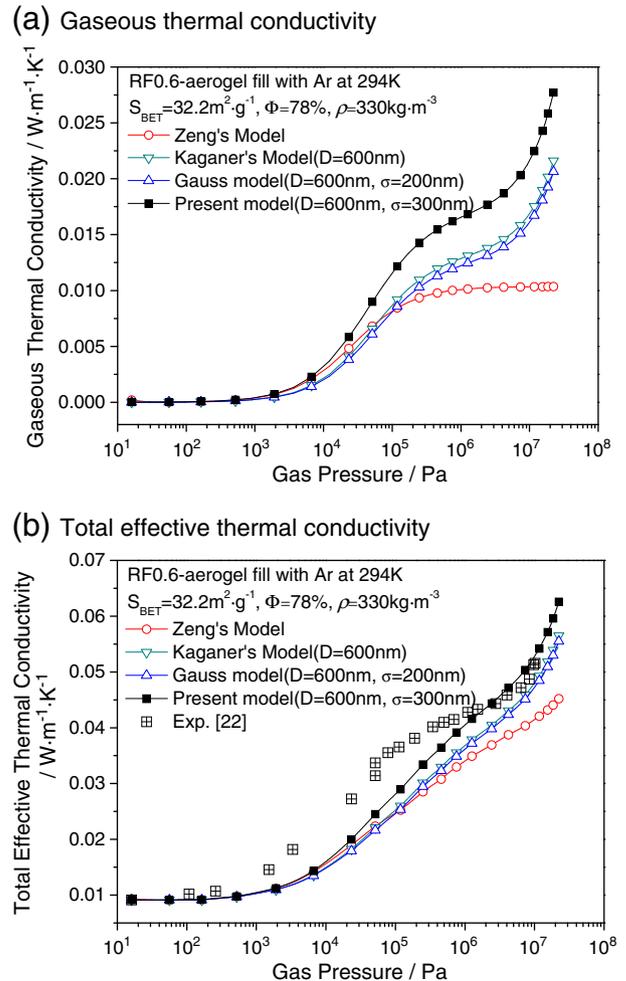


Fig. 7. Gaseous and total effective thermal conductivities in organic aerogel.

the gaseous thermal conductivity. The results predicted by Zeng's Model deviate much from those by the other models when the gas pressure exceeds 0.2 MPa, because Zeng's Model does not consider the real gas effect, i.e. that the gas thermal conductivity increases with the increase of the gas pressure.

The total effective thermal conductivity of the material is the superposition of the solid thermal conductivity (λ_s), the gaseous thermal conductivity (λ_g), the radiative thermal conductivity (λ_r), and the coupling thermal conductivity (λ_c) [22]. We assume that the predicted thermal conductivities of λ_s , λ_r and λ_c in Ref. [22] are accurate enough, and then replace λ_g calculated by Kaganer's Model in the literature with the one predicted by the present model. The obtained total effective thermal conductivities are presented in Fig. 7(b) in comparison with the available experimental data. We can still find the deviations between the theoretical models and experimental data, but the results calculated by the present model are more close to the measured data. As for the errors, Ref. [22] ascribed the deviations to the coupling effect and the measurement uncertainties of the pore-size and particle size.

4. Further discussion

From the above analysis, we can find that the present model with respect to Eqs. (6) and (10) can significantly improve the prediction accuracy for the gaseous thermal conductivity. More importantly, the present model can be applied to all the types of the aerogels in Section 3 while other models fail.

Note that the present model is a modified model with several assumptions based on the Kaganer's Model, so its accuracy needs to be improved further. In fact, the pore-size distribution of some aerogels can be obtained by the experimental measurement, such as the BJH method or Non-Local Density Functional theory (NLDFT) from the nitrogen or argon sorption, but it just reflects the pore volumes (e.g. Fig. 8) of different pore-sizes rather than the contributions (i.e. Φ_i in Eq. (6)) of the pore-sizes to the total porosity of the porous material. Imagine that a rational distribution function (Φ_i), transformed from the BJH or NLDFT adsorption pore-size distribution, probably describes the contribution of the pore-size to the total porosity more accurately than Eq. (7) or Eq. (10). Similar to the pore-size distribution shown in Fig. 8, we can use a simple expression to estimate Φ_i based on the BJH data:

$$\Phi_i \approx \frac{f(D_i)}{\int_{D_{\min}}^{D_{\max}} f(D') dD'} \approx \frac{f(D_i)}{\sum_{j=1}^{j_{\max}} f(D_j) \Delta D_j} \quad (15)$$

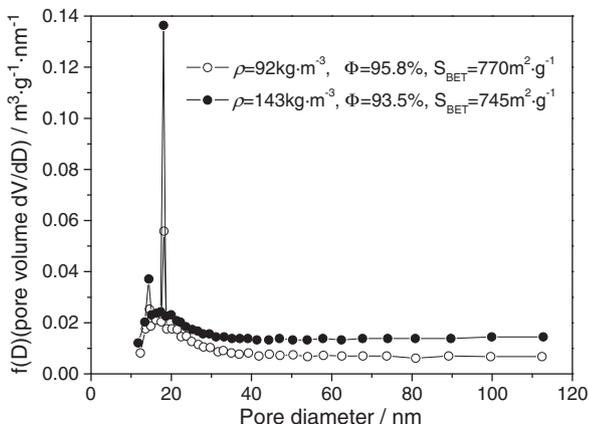


Fig. 8. BJH adsorption pore-size distribution for silica aerogels [23].

where $f(D)$ refers to the distribution function of the pore-size from the BJH method, i and j are the indexes corresponding to the measuring points, ΔD_j is the difference between D_j and D_{j+1} . However, note that the gaseous thermal conductivity predicted by Eqs. (10) and (15) still needs to be verified by a large number of experimental data.

5. Conclusions

In this study we have proposed a modified model based on the Kaganer's Model to improve the prediction accuracy of the gaseous thermal conductivity. In the model, a pore-size distribution function is introduced to take into account the effects of the random and non-uniform pore-size distribution in the actual aerogels, and thus the prediction accuracy is greatly improved. The present model is convenient and easy to calculate the gaseous thermal conductivity in the aerogels since it is based on the Kaganer's Model which is easy to calculate the gaseous thermal conductivity in the aerogels. Both available experimental data in the literature and other theoretical models were employed to verify the present model, and the present model is proved to have the best accuracy to predict the gaseous thermal conductivity for various types of nano-porous aerogels. Nevertheless, the accuracy of the present model still needs to be further verified by more experimental data. In addition, some large deviations exist between the experimental data and the calculated results by the theoretical models, and one of the most important reasons can be attributed to the coupling effect, especially in the organic aerogel and fumed aerogel.

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