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Predicting the thermal conductivity of porous building materials with nanopores or reduced gas pressures

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ABSTRACT
Porous materials with nanopores or reduced gas pressures like aerogels, nanocellular foams or vacuum insulation panels show a great potential as insulation materials, due to their extremely low thermal conductivity. Understanding the relation between their pore structure parameters and effective thermal conductivity is crucial for further optimization. This paper discusses the extension of a numerical framework simulating the heat transfer directly at the material's pore scale. A novel methodology to model the reduced gaseous conductivity in nanopores or at low pressures is presented, accounting for the three-dimensional pore geometry while remaining computationally efficient. Validation with experimental and numerical results from literature indicates the accuracy of the methodology over the full range of pore sizes and gas pressures. A simple case study is analysed, which shows the expected improvements of the thermal conductivity when reducing the pore size for materials with different porosities. The numerical framework thus offers the possibility for a more thorough understanding and optimization of the thermal conductivity of superinsulators.

KEYWORDS
Thermal conductivity; porous materials; superinsulators; nanopores; low-pressure

INTRODUCTION
Heat losses through opaque building components like walls and roofs account for a large part of the total heating demand in buildings. Hence, porous insulation materials are often applied, offering a relatively low thermal conductivity due to their porous nature (Smith et al., 2013). To comply with progressively stringent energy requirements though, increasingly large insulation thicknesses are needed, hindering the design and the refurbishment of new and existing buildings. In the search for better performing insulators, a promising solution is offered by materials having pores with diameters in the nanoscale range and/or with reduced gas pressures inside. Examples are aerogels or aerogel-based materials (Baetens et al., 2011), nanocellular foams (Liu et al., 2015) and vacuum insulation panels (Jelle et al., 2010). Research has shown that in these materials the gaseous conduction shifts from the Fourier to the Knudsen regime, resulting in a reduced gaseous and hence overall effective thermal conductivity (ETC) (Jelle et al., 2010). Furthermore, the effect becomes even more crucial at increasing material porosities where conduction through the gaseous phase becomes progressively more dominant in the total heat transfer (Solórzano et al., 2009). Modelling efforts so far though have mainly focussed on obtaining analytical expressions, predicting the ETC as a function of several pore scale parameters like porosity and pore size (He & Xie, 2015; Wang et al. 2017). A more detailed understanding of the pore structure influence on the total ETC is hence needed to improve their performance significantly. To this aim, a numerical framework was recently implemented predicting the ETC of porous building materials based on their pore structure. A 3D voxel image representation of the microstructure, obtained via either micro-CT scanning

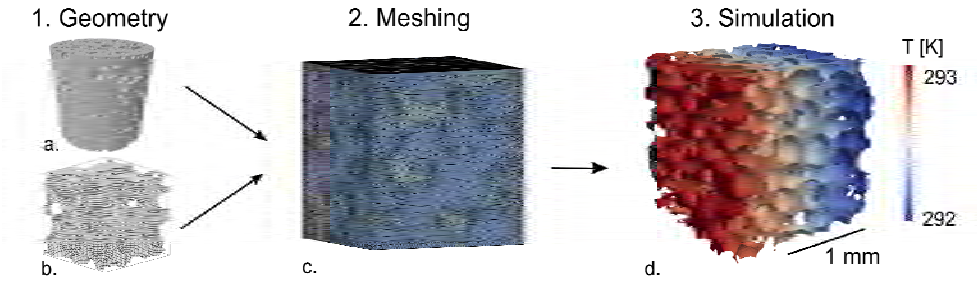

Figure 1: The numerical framework simulates the pore scale heat transfer to deduce the ETC. (a) micro-CT image of cellular concrete; (b) virtual material; (c) finite element mesh; (d) temperature profile.

or virtual generation, is used as input for the pore scale heat transfer simulation (Figure 1); more details can be found in the paper by Van De Walle & Janssen (2016). Currently, the model framework is limited though to porous materials with pore dimensions above several micrometres and containing gas at atmospheric pressure. Extension to a physical description of the Knudsen effect on the gaseous conductivity could enlarge its scope and facilitate the characterization of possible optimization strategies for superinsulating materials.

This paper discusses the implementation of the dimension- and pressure-dependent gaseous conduction in the aforementioned numerical framework. A novel simulation methodology based on the kinetic theory is introduced to obtain the local gaseous conductivities, offering an efficient calculation procedure while taking into account the pores' specific geometry. The proposed methodology is validated with experimental and numerical results from literature. Finally, the model is applied in an exploratory case study to investigate the effect of the pore size at different material porosities. Currently, only materials in dry conditions are targeted.

GASEOUS CONDUCTIVITY

The kinetic theory framework is used to model the microscopic gaseous heat transfer in pores. Firstly, the general theory is revisited for clarity, then the extension to reduced dimensions and/or gas pressures is explained. Finally, the implementation of the methodology in the numerical framework is discussed.

General kinetic theory

The kinetic theory framework allows to describe the heat conduction through gas as a function of the gas properties. Apart from the density ρ_{gas} [kg/m³], the specific heat capacity at constant volume $c_{V,gas}$ [J/kgK] and the mean molecule speed v_{mean} [m/s], the gaseous thermal conductivity depends on the mean free path L_{MFP} [m], which is the average distance a gas molecule travels before colliding with another gas molecule (eq. 1), (Zhang, 2007; Jiji, 2009).

$$q_{cond} = -\frac{1}{3} \cdot \rho_{gas} \cdot c_{V,gas} \cdot v_{mean} \cdot L_{MFP} \cdot \frac{dT}{dx} = -\lambda_{gas,bulk} \cdot \frac{dT}{dx} \quad (1)$$

Here, q_{cond} [W/m²] is the total heat flow caused by the temperature gradient dT/dx [K/m], and $\lambda_{gas,bulk}$ [W/mK] is the bulk gaseous thermal conductivity. The mean free path between successive collisions depends on the temperature and pressure of the gas, as well as on the gas molecule properties. However, as argued by Jiji (2009), the mean free path between collisions is not completely suited to describe the energy transport, since it doesn't consider the efficiency of energy exchange between two colliding particles. Therefore the 'energy' mean free path was introduced, which should be used in eq. 1 to obtain correct results. This energy mean free path can easily be deduced for bulk gases by reverse calculating equation 1, leading for example to an energy mean free path of 180 nm for air at 20 °C and atmospheric pressure.

Apart from gaseous heat conduction, the kinetic framework can equally be applied to describe heat conduction in solids by electrons, phonons (acoustic waves), and radiative heat transfer by photons (electromagnetic waves), considering the waves as particles (Chen, 2005). Although less accurate than more detailed simulation strategies like molecular dynamics or lattice Boltzmann simulations, the kinetic theory is capable of predicting reasonably well the thermal transport and thermal conductivity. This paper focusses solely on the implementation for gaseous conduction.

Extension to pore cavities with reduced dimensions and gas pressures

When the pore dimensions or gas pressure start to reduce, gas particles start colliding relatively more often with the pore boundaries instead of with each other, which is called the Knudsen effect. This translates to a reduction in the effective mean free path of the molecules and - according to eq. 1 - to a reduction of the gaseous conduction. The effective mean free path can be calculated according to Matthiessen's rule, combining the bulk mean free path and the mean free path induced by the boundaries, as shown in eq. 2 (Jiji, 2009).

$$\frac{1}{L_{MFP,eff}} = \frac{1}{L_{MFP,bulk}} + \frac{1}{L_{MFP,bdy}} \tag{2}$$

Again, the effectiveness of energy exchange between molecules and boundaries will influence the thermal transport. This is usually described with the thermal accommodation coefficient a, varying between 0 and 1, and very similar to the better-known absorptivity coefficient α used in thermal radiation simulations (Zhang, 2007; Jiji, 2009). Hence, an 'energy' boundary mean free path should be defined including this factor, thus directly incorporating the boundary resistance effect. Apart for simple structures like parallel plates, accurate calculation of this energy boundary mean free path is far from trivial. A novel method is therefore implemented in the model framework to account for the real 3D geometry of pores.

Including nanoscale gaseous conduction in the model framework

To calculate the gaseous conductivity in each pore, the energy boundary mean free path needs to be determined. A calculation methodology based on the analogy with radiative heat transfer is proposed, simplifying the simulation procedure. Introduced by Loeb (1954) and later extended by Van De Walle & Janssen (2016), the radiative heat transfer in a pore cavity can be described as a conductive process with a radiative conductivity depending – amongst others – on the pore dimensions and the wall's absorptivity. The formulas proposed by Van De Walle & Janssen (2016) to calculate this conductivity are shown in eq. 3 and 4. Eq. 3 is equalized to the more general form of the radiative conductivity originating from the kinetic theory.

$$\lambda_{rad,pore} = 4 \cdot \sigma \cdot T^3 \cdot d_{mean} \cdot C(\alpha, S_f) = \frac{1}{3} \cdot 16 \cdot \sigma \cdot T^3 \cdot L_{MFP,rad,eff} \tag{3}$$

$$S_{f,2D} = h_{mean} / d_{mean}; S_{f,3D} = h_{mean} \cdot w_{mean,} / d^2_{mean} \tag{4}$$

Here, T [K] is the average temperature inside the pore, σ [W/m^{2}K^4] the Stefan-Boltzmann constant and d_{mean}, h_{mean} and w_{mean} [m] the mean distance between opposing pore walls parallel (d_{mean}) or perpendicular (h_{mean}, w_{mean}) to the heat transfer direction. $C(\alpha,S_f)$ [-] is a factor taking into account the effect of the absorptivity and the geometry of the pore walls using the directional slenderness factor S_f [-], and was defined based on a series of radiative simulations in several pores with varying geometries (Van De Walle & Janssen, 2016).

Since the bulk mean free path of photons $L_{MFP,rad,bulk}$ travelling in a non-absorbing medium like air is considered very large (~kilometres), the effective mean free path reduces to the boundary mean free path. Indeed, radiation is often modelled as only depending on the system boundaries. Using the analogy between gas particles and photons as well as between the thermal accommodation coefficient and the absorptivity, we can rewrite the last two parts from eq. 3 to finally formulate an expression calculating the energy boundary mean free path for gas particles in a certain pore (eq. 5).

$$L_{MFP,bdy,en} = \frac{3}{4} \cdot d_{mean} \cdot C(a, Sf) \tag{5}$$

Here, a is now the thermal accommodation coefficient instead of the radiative absorptivity. Hence, combining eq. 5, 4, 2 and 1, the reduced gaseous conduction can be calculated for every pore, knowing the gas state (pressure and temperature), the bulk gas properties (R_s [J/kgK], $c_{V,gas}$ and $\lambda_{bulk,gas}$) and the material properties (pore dimensions and thermal accommodation coefficient).

VALIDATION OF GASEOUS CONDUCTION CALCULATION

The implemented gaseous conductivity calculation procedure is validated against experimental and numerical results found in literature for different geometries, gasses and thermal accommodation coefficients.

Gas confined between parallel plates

The accuracy of the implemented calculation procedure to predict the gaseous conductivity variation is examined firstly for the simple case of parallel plates. Results are compared with experimental measurements of Braun & Frohn (1976) on Ar gas at pressures from 8.5 Pa to 66735 Pa, and with numerical DSMC simulations by Denpoh (1998) on N_2 gas at plate separation distances from 1.6 nm till 22 μm. Details of both studies are summarized in Table 1, results are brought in Figure 2a. For both cases, the calculation procedure proves to accurately predict the gaseous thermal conductivity over the whole range of pressures and plate separation distances, even at varying thermal accommodation coefficients. Furthermore, they agree also very well with the often applied analytical prediction formula of Zhang (2007), derived for heat transfer between parallel plates.

Cuboid nanopore

The gaseous conductivity in real, more complex shaped pores depends (apart from the pore size and gas pressure) also on the pore's specific geometry. The performance of the novel calculation procedure – able to take the three-dimensional shape of the pore into account – is validated on a cuboid nanopore. Predicted results are compared with numerical DSMC simulations performed by Zhu et al. (2017) on Ar gas in a cuboid pore, varying the side length from 24 nm till 1.4 μm; details are mentioned in Table 1. The gaseous conductivity predicted by our model agrees very well with the simulation results of Zhu et al. over the whole range of pore sizes, see Figure 2b. Furthermore, the model clearly outperforms the parallel plates formula of Zhang, underlining the importance of taking the true pore geometry into account.

Table 1. Properties used in the model to predict the gaseous thermal conductivity (NIST).

Study	Geometry	Gas	$\lambda_{gas,bulk}$ [W/mK]	a [-]
Braun & Frohn, 1976	// plates	Ar @ 323 K	0.0188	0.7385
Denpoh, 1998	// plates	N_2 @ 343 K	0.0286	0.1 – 0.5 – 1
Zhu et al., 2017	Cuboid	Ar @ 300 K	0.0177	1

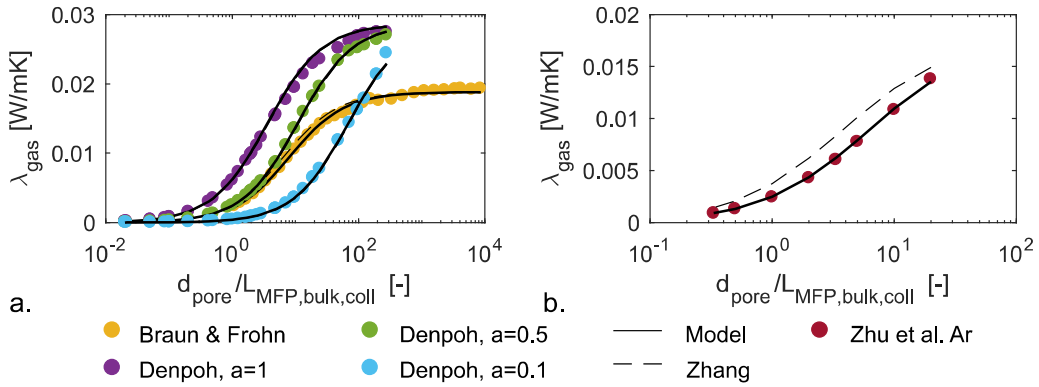

Figure 2: Gaseous conductivity results predicted by our model agree very well with experimental and numerical literature for gas confined between parallel plates (a) and gas in a cuboid nanopore (b).

CASE STUDY

Lastly, a case study is performed to investigate the potential impact of reducing the pore size and thus the gaseous conductivity on the total ETC of a porous sample. A body-centred cubic (BCC) unit cell is used as sample pore structure, considering the spheres as air-filled cavities inside a solid matrix. Three different material porosities are considered (50 %, 70 % & 90 %). The thermal conductivity of the matrix is set to 1 W/mK, simulations are performed at 20 °C mean temperature and 101325 Pa air pressure inside the pores. The specific heat capacity at constant volume is assumed to be 717 J/kgK (NIST), while a common value of 0.9 is taken for the thermal accommodation coefficient (Zhang, 2007). First, the ETC of each sample is calculated setting the pores' diameter to 1 mm, hence having the bulk air thermal conductivity inside them. Subsequently, the dimensions of each sample are rescaled five times, obtaining five different pore diameters between 1 nm and 10 µm. The total ETC of each sample is calculated using the numerical framework described in the introduction, taking into account the reduced gaseous thermal conductivity in every pore. The effect of the pore dimensions on the effective matrix conduction and radiative heat transfer is not taken into account here. A resolution of 400^3 for the voxel grid image is applied together with a mesh size of 3 times the respective voxel size, showing no further improvement with increasing grid and mesh refinement. As expected, the ETC generally decreases with increasing porosity and decreasing pore diameter (Figure 3). Furthermore, the effect of the pore size becomes more pronounced at increasing porosities, since gaseous conduction becomes progressively more dominant in the total heat transfer. The steepest drops are observed when decreasing the pore size from 10 µm to 100 nm, resulting in an ETC decrease of over 30 % for the sample with 90 % porosity. However, at the relatively high matrix conductivity involved here, the sample's porosity seems to remain the most important parameter. Future research will focus on studying

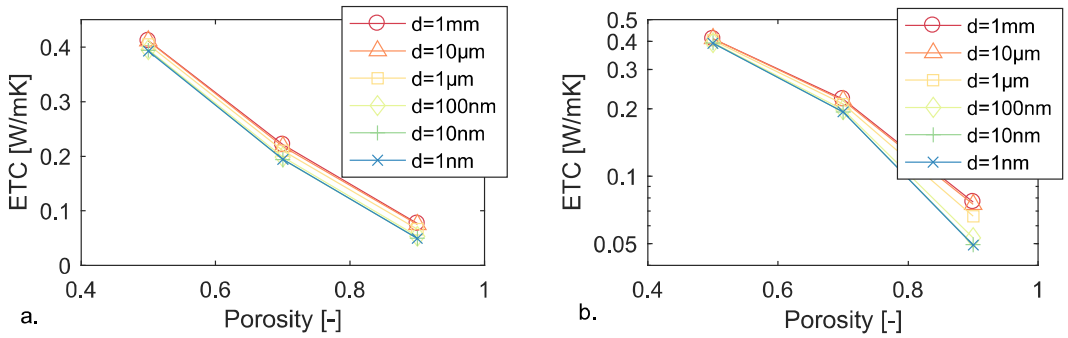

Figure 3: The ETC decreases with increasing porosity and decreasing pore size (a); at higher porosities the effect of a smaller pore size becomes more pronounced (b).

more complex materials and including the nanoscale effect on the matrix conduction and the radiative heat transfer in nanoporous materials.

CONCLUSIONS & FUTURE WORK

The paper presents the extension of a numerical framework to study the heat transfer in porous insulation materials showing low thermal conductivities due to the Knudsen effect. A novel computationally efficient method for calculating the gaseous conductivity in nanopores and at reduced gas pressures is discussed and validated against experimental and numerical results found in literature. An exploratory case study showed the effect of reduced pore dimensions on the ETC of a porous material, at three different porosities. Future work will focus on validating the model with experimental measurements on real materials having nanopores or reduced gas pressures.

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