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Correlation between the elastic modulus and heat transport along the solid phase in highly porous materials: Theoretical approaches and experimental validation using polyurea aerogels

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ABSTRACT

The elastic modulus and solid phase thermal conductivity were experimentally determined for two series of supercritically dried polyurea aerogels. Both sample series cover a density range between 0.03 and 0.3 g/cm^3, respectively, while micro-structural details of the aerogels are completely different for the samples of the two series, thus leading to considerable differences in macroscopic properties, when comparing two samples from the two series at a given density. On the contrary, elastic modulus is found to strongly correlate with the heat transport along the solid phase, irrespective of the sample series considered. The insensitivity of this correlation to micro-structural details can be explained with theoretical approaches that are used to describe the macroscopic properties of porous materials. However, also possibilities for a structural decoupling of the elastic modulus and the heat transport along the solid phase could be identified that may open new approaches for technical applications.

1. Introduction

Because of their particular material properties porous materials are found in numerous technical applications such as lightweight constructs, thermal insulation, catalysis and filters. Moreover, the properties of this material class are highly designable. Respecting the limits of manufacturability, three parameters are available to tailor the macroscopic properties of a porous material: the non-porous backbone material, the bulk-density of the material (porosity) and the structural organization of the backbone-structure. The latter is of special interest for technical applications, as hereby, properties can be changed without modifying the materials density.

This study focuses on the question if the elastic modulus and the thermal conductivity that is based on the heat transport via the solid phase, show the same sensitivity on the geometrical details of the micro-structure. Thermal conductivity and the elastic modulus render a material interesting, e.g., for an application as a thermal insulation material. Insulations based on nano-porous materials show a superior thermal conductivity of 0.012 mW/mK that is mainly due to the heat transport via the solid phase [1]. On the other hand, the mass-normalized mechanical stiffness of these materials are low, too, restricting the field of technical application [2]. In this case, it would be of major interest, if the elastic modulus can be increased while keeping the thermal conductivity of the material low (decoupling of these two properties).

In the framework of this study, the macroscopic elastic modulus and thermal conductivity along the solid phase are experimentally derived for two series of polyurea (PUA) aerogels. The sample series offer a great variety in structural details and render them interesting to analyze both, the impact of a structural detail on the macroscopic property and the correlation between the elastic modulus and the solid thermal conductivity in terms of structural features. Experimentally derived results are further correlated to theoretical models that are used to describe the macroscopic properties of porous materials. While extensive studies have been performed on the relation between structural details and macroscopic properties in porous materials, an in-depth experimental analysis for the correlation between the elastic modulus and the thermal conductivity has not been published yet.

2. Theoretical approaches to derive the macroscopic properties of porous materials

For modelling the macroscopic properties of porous materials, three approaches can be found in literature.

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Nomenclature

Symbol	
c_{11},c_{44}	Elastic constants
C_1,C_2	Constants referring to the geometrical arrangement within a unit-cell
E	Young's modulus
$E0$	Young's modulus of the non-porous backbone material
$p$gas	Gas pressure
$(p-pc)$	Site percolation
vl	Velocity of a longitudinal ultrasonic wave
αAerogel	Scaling exponent for the thermal conductivity of aerogels
βAerogel	Scaling exponent for the elastic modulus of aerogels
κ	Effective adiabatic exponent of the pore gas
$\lambda 0$	Thermal conductivity of the non-porous backbone material
λsolid	Thermal conductivity along the solid framework
ν	Scaling exponent for the cluster correlation length
$\prod$	Porosity
ξ	Cluster correlation length
$\rho 0$	Density of the non-porous backbone material
ρ	Density

2.1. Unit-cell model for regular structures

The first and most intuitive approach is based on the idea that the structure of a highly porous material can be represented by a periodical arrangement of *unit-cells* [3]. Within a *unit-cell*, the network-elements (named *struts*) are organized in a geometrical arrangement so that the macroscopic properties of the cell and that of the porous material, respectively, can be analyzed analytically. As the thermal resistance of a *unit-cell* solely depends on the thickness and length of the struts, thermal conductivity λ_{solid} is found to scale linearly with density ρ [4,5]:

$$\frac{\lambda_{solid}}{\lambda_0} = C_1 \frac{\rho}{\rho_0} \tag{1}$$

The constant C_1 depends on the geometrical arrangement within a *unit-cell* and is strongly correlated to the relative amount of material oriented in the direction of the heat flow. Macroscopic properties are furthermore defined by the properties of the non-porous material (marked with the index 0).

For the resistance versus mechanical deformation, it is found that struts are predominantly bent, if a mechanical load is applied to the *unit-cell* [3,6–9]. Taking into account the boundary conditions for the struts that are given by the geometrical arrangement, the elastic modulus of the *unit-cell* can be calculated from the applied force F (stress σ) and the observed deformation δ (strain ϵ). As the deformation δ of a strut depends on its moment of inertia, the Young's modulus E of the cell is ascribed to the thickness -to-length-ratio (t^4/l^4) of the struts and therefore quadratically scales with density [3]:

$$\frac{E}{E_0} = C_2 \left(\frac{\rho}{\rho_0}\right)^2 \tag{2}$$

The constant C_2 depends on the geometrical arrangement of the *unit-cell* and on the cross-section geometry of the struts, respectively.

While the basic *unit-cell* model successfully predicts the macroscopic properties of highly porous materials that are characterized by a regular microstructure (e.g., honeycombs or foams), scaling laws of porous materials with irregular microstructure (e.g., statistically isotropic) significantly deviate from the linear and quadratic dependency found in Eqs. (1) and (2). For aerogels, the heat transport along its solid framework is rather found to scale with an exponent $\alpha_{Aerogel}$ of 1.2–1.5 and the elastic modulus scales with an exponent $\tau_{Aerogel}$ of 2.4–4 [10,11]:

$$\lambda \propto \rho^{\alpha} \quad \alpha_{Aerogel} > 1 \tag{3}$$

$$E \propto \rho^{\tau} \quad \tau_{Aerogel} > 2 \tag{4}$$

The *unit-cell* model can explain the exponents $\alpha_{Aerogel}$ and $\tau_{Aerogel}$ derived, if the prefactors C_1 and C_2 change with density.

A geometrical arrangement that can be used as a *unit-cell* to characterize the micro-structure of an aerogel is given by the *nodes-links-blobs* model [12]. Within the *nodes-links-blobs* model it is considered that the backbone of an aerogel consists of parallel network elements (*blobs*) that are connected via single connection bonds (*links*) to form clusters of different size. Furthermore, a part of the backbone elements is attached to the backbone-structure on one end only (*dangling bonds*). If both, the fraction of *dangling bonds* and the tortuosity[1] of the network paths changes with density, both, the macroscopic properties of aerogels and the scaling laws $\alpha_{Aerogel}$ and $\tau_{Aerogel}$, respectively, can be explained theoretically [13,14].

2.2. Percolation theory

Alternatively to the *nodes-links-blobs* model, the irregular but not fully statistically backbone structure of an aerogel can be computationally derived by using diffusions-limited cluster algorithms (discrete model systems) or the *Swiss-cheese* model (continuous model system) [15]. The structural information gained by these models focuses on how *dangling bonds* and *links* or rather on how the strut thickness vary with site percolation, i.e., the parameter $(p-p_c)$ (i.e., with density[2]). The impact of structural details on the macroscopic property can be calculated taking into consideration the thermal conductivity and the elastic force constants of a single network elements (*bonds*) and transferring them stepwise onto the meso-scale network-elements (*cluster*, *chain*) and the macroscopic level, respectively. As the thermal conductance of an network element only depends on the length and thickness of network-element, whereas the elastic force constant strongly depends on both, the geometry of a *cluster* (arrangement of *blobs* and *links* within the cluster) and the direction of the applied force, two different Hamiltonians should be used to calculate the thermal and mechanical properties, respectively [16]. It is found that the macroscopic elastic modulus E and the thermal conductivity λ_s of percolating systems are correlated to the length of the largest cluster within the system (*cluster correlation length* ξ) and scaling laws, in turn, can be expressed as a function of the scaling exponent ν found for the *cluster correlation length* ξ [16,17].

$$\xi \propto (p-p_c)^{-\nu} \tag{5}$$

$$\lambda_s \propto (p-p_c)^{\nu+1} \tag{6}$$

$$E \propto (p-p_c)^{3\nu+1} \tag{7}$$

The varying strut thickness of a continuous percolating system (*Swiss-cheese* model) increases the power law exponent of the conductivity to $(\nu+1.5)$ and the power law exponent of the elasticity to $(3\nu+3.5)$ [18,19]. Besides, it is found that in a percolating system

[1] The tortuosity describes the detour factor of a path within a cluster normalized to the linear distance between two points.

[2] For low percolation thresholds p_c the parameter $(p-p_c)$ equals the density of a real material.