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1999 J. Phys.: Condens. Matter 11 7971

(http://iopscience.iop.org/0953-8984/11/41/302)

J. Phys.: Condens. Matter **11** (1999) 7971–7976. Printed in the UK PII: S0953-8984(99)03320-2

A percolation approach to aerogel gas permeability

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Received 8 April 1999, in final form 14 July 1999

Abstract. We performed a numerical and theoretical study of the critical behaviour of the permeability to gases in aerogels of different densities. In order to compute the critical exponent, it has been necessary to calculate the percolation critical density for densifying aerogels. As a final result, the permeability critical exponent is found to be different to that of random media. The theoretical and numerical results agree very well.

1. Introduction

Silica aerogels are very light porous materials which exhibit a fractal structure. When heated to a temperature close to the glass transition temperature, aerogel pores narrow and close; and the aerogels transform into dense silica glass.

Flow, dispersion and displacement processes in natural porous media arise in many diverse fields of science and engineering. We study here the permeability to gases of aerogels with different densities. The permeability is defined as the pore volume multiplied by the diffusion constant of the gas flowing through the aerogel. To study aerogel gas permeability, one has to deal with complex pore structure. Indeed, the aerogel pore structure differs from rock pore structure, as pores in aerogels exhibit a space correlation due to the silica structure space correlation itself. It is at present not clear whether the permeability, as we define it here, is affected by the pore distribution or by the fractal structure of the matter in the aerogel.

If it is the fractal structure of matter which affects the diffusion constant and consequently the permeability, we may relate this study to former studies made on porous media. Indeed, if the diffusion constant is affected by the fractal structure of matter, i.e. if the aerogels are macroscopically heterogeneous, we may expect the critical exponent of the permeability to depend on the size of the fractal domain.

There have been several studies on rock and aerogel permeability to gases and fluids [1–3]. In a rock, the pore network may be roughly modelled by holes with random sizes, locations and directions (i.e. shapes). If the pore distribution is random, and if the long-range correlations are negligible, transport in a porous medium is analogous to a random-resistances lattice, i.e. related to a percolation problem. For this kind of random distribution of pores, one would anticipate a universal behaviour of the permeability which would depend only on the Euclidean space dimension. In contrast, in aerogels, the pore network exhibits a long-range correlation which will probably induce different critical characteristics on approaching the pore percolation aerogel density. This study plans to show whether it is the pore distribution which affects the permeability, or the fractal structure of matter which modifies the gas diffusion constant.

So, when the density of the aerogels increases (by densification) for a given initial density, the gas can no longer flow through the sample and the permeability tends to zero: the aerogel is then no longer permeable. Here, we will call this value of the density the percolation density or critical density, as for percolation problems (indeed, when the aerogel is no longer permeable, the pores no longer percolate). As for percolation problems, it is possible to compute a critical exponent κ_p for the behaviour of the permeability. It is essential for this study to calculate first the critical concentration at which the aerogel ceases to be permeable to gas. We study here the dependence of the critical density at which the pores cease to percolate on the initial density, for densifying aerogels. Then different critical exponents will be computed: for the pore size and for the permeability near the percolation transition. With the critical behaviours (near the critical density) of the pore size, of the gas diffusion constant and of the permeability, we will reach a conclusion as to which characteristic of the aerogel affects the behaviour of the permeability. In the following we will use concentration and density interchangeably for the mass/volume ratio in the aerogel.

2. Theory

2.1. Critical concentration

Following recent scaling theories, the sintering of silica aerogels is modelled starting from computer-generated gel structures obtained by diffusion-limited cluster–cluster aggregation (DLCA) on a cubic lattice [4, 5]. Two steps compose the sintering process model: a 'dressing' step in which all particles are replaced by overlapping larger particles and a 'contraction' step in which an appropriate length rescaling is performed in order to conserve the total mass. Here, we will call the rescaling factor β. As been found numerically by Olivi-Tran and Jullien [6], the evolution of the critical concentration c_{crit} at which the pores cease to percolate is a function which decreases when the initial concentration c_0 of the aerogel increases. From a theoretical point of view, we may calculate this critical concentration as a function of the initial concentration of the non-densified aerogel. The mean size of the pores can be approximated by $(1-c)^{1/3}$, where c is the concentration at a given stage of densification. In fact, this mean size becomes critical when the mean size of the pores is equal to the mean size of the pores in the aerogel of initial concentration $1-c_p$, where c_p is the concentration of the site percolation threshold in three dimensions. Sempere *et al* [6, 7] used a contraction coefficient to link two different stages of the aerogel density during densification. This coefficient is simply the cube root of the rate between the initial aerogel density c_0 and the density c. For example, the size a of the particles composing the aerogel at a given stage of densification is related to the initial size a_0 of the particles (before densification) by $a \propto a_0\beta$, where $\beta = (c/c_0)^{1/3}$.

In our sintering model, a characteristic length L_0 of the initial stage (before densification has begun) and a characteristic length L of a stage of concentration c are related by $L \propto L_0\beta$, where β is the rescaling factor which links two consecutive stages of aerogel sintering.

So, the mean size of the pores at the percolation transition is $(1-c_p)^{1/3}/\beta$, with $\beta = (c/c_0)^{1/3}$. In this procedure, we obtain the initial concentration c_0 of the aerogel as a function of the critical concentration c_{crit} and the percolation concentration for three-dimensional random packings c_p:

$$c_0 \propto \frac{1-c_{crit}}{1-c_p}\frac{1}{c_{crit}}. \tag{1}$$

So we have a relation between the percolation concentration c_p (which may be found in the literature for a cubic lattice), the initial concentration c_0 of the aerogel before densification has begun and the critical c_{crit} that we look for. This relation allows one to calculate this critical concentration at which the gas particle diffusing in the material can no longer flow through it.

2.2. Permeability; the mean-field approach

The diffusion constant for the gas particle diffusing in the aerogel may be computed from $D \propto \ell^2/\Lambda$, where ℓ^2 is the mean square displacement and Λ is the end-to-end total length of the trajectory. So, ℓ^2 (due to the mean size of the accessible pores) may be approximated by

$$\ell^2 \propto (c_{crit} - c)^{2/3} \tag{2}$$

where c is the concentration (density) of the aerogel at a given stage of densification. Then Λ may be computed assuming that the number of collisions with the walls of the pores is inversely proportional to the specific surface Σ of the material:

$$\Lambda \propto (c_{crit} - c)^{1/3}/\Sigma. \tag{3}$$

An easy calculation gives the diffusion constant D:

$$D \propto (c_{crit} - c)^{1/3}\Sigma. \tag{4}$$

In order to compute this diffusion constant, we need to know the value of the specific surface. As can be found in reference [6], the specific surface is given by the formula

$$\Sigma \propto \frac{\mathrm{d}\log c(s)}{\mathrm{d}s}\beta(s) \tag{5}$$

where $\beta(s)$ is the contraction factor:

$$\beta(s) = \left(\frac{c(s)}{c_0}\right)^{1/3} \tag{6}$$

where $c(s)$ is the concentration of the aerogel at a given stage of densification determined by the size of the particles composing the aerogel, a_s:

$$a_s = a_0 \frac{1+s}{\beta(s)}. \tag{7}$$

This method has been extensively described in reference [6]. So finally the permeability (which is the accessible pore volume multiplied by the diffusion constant) becomes

$$K(s) \propto \frac{c_{crit} - c}{\beta^2(s)} D \tag{8}$$

where $(c_{crit} - c)/\beta^2(s)$ is the accessible pore volume. We obtain then, the permeability:

$$K(s) \propto [(c_{crit} - c(s))^{4/3}/c(s)^{1/3}]\, \mathrm{d}\log c(s)/\mathrm{d}s. \tag{9}$$

Here, all of the lengths which have been used are *accessible lengths*, i.e. the average calculated length characteristic of the open pores of the sample. To calculate the critical exponent of the evolution of the permeability near the percolation threshold for the densified aerogel, we use equation (9) giving the permeability as a function of the concentration. If the difference between the concentration and the critical concentration c_{crit} is ϵ (i.e. $c = c_{crit} - \epsilon$), one can rewrite equation (21) as follows:

$$K \propto \frac{(\epsilon)^{4/3}}{(c+\epsilon)^{1/3}} \frac{1}{c+\epsilon} \frac{\mathrm{d}(c+\epsilon)}{\mathrm{d}s}. \tag{10}$$

An easy calculation gives a critical exponent equal to 4/3.

2.3. Permeability; the pore chord distribution approach

In this last approach, we do not take account of the fractal structure of the aerogel. Following Levitz [8, 9], we will use the pore chord distribution. The pore chord distribution may be defined as the number of segments linking two particles composing the aerogel as a function of the segment length r. Levitz found that the probability of going from one point of the pore network to the pore wall along a finite section of a segment inside the pore is

$$\Psi_{p,i} = [\delta(r-t)/(4\pi r^2\langle l_p\rangle)]\int_r^\infty 1/r'^{D_f-1}\,\mathrm{d}r' \tag{11}$$

where $\langle l_p\rangle$ is the first moment of the pore chord distribution.

The ballistic propagator G_b for the gas particle motion is

$$G_b(r,t) = [\delta(r-t)/(4\pi r^2)]\left(1-\int_0^t \mathrm{d}t'\int_0^r 4\pi r'^2\Psi_{p,i}(r',t')\,\mathrm{d}r'\right). \tag{12}$$

$G_b(r,t)$ is a propagator, which may be defined as the probability of moving, during a time interval t, from the interface of one pore to another interface.

So the mean square displacement in the porous medium, i.e., the second moment of the ballistic propagator, becomes, after some calculations involving equations (11) and (12),

$$\langle r^2\rangle \propto \Lambda'^{-2D_f+6} \tag{13}$$

where Λ' is a given length proportional to the size of the aerogel fractal domain—equivalent to a time if the velocity is equal to 1, and hence equivalent to the total length of the trajectory Λ. In this case, it is not possible to calculate a diffusion constant D, as the ratio $\langle r^2\rangle/\Lambda'$ diverges with Λ'. Anyway, here we will define the permeability in the same way as we did in the mean-field approach, i.e. the permeability is the accessible pore volume multiplied by the ratio $\langle r^2\rangle/\Lambda'$ where $\langle r^2\rangle$ is the mean square displacement and Λ' is the time (equivalent to the total length of the trajectory). This feature allows one to compare the numerical results with this theoretical result, as the definition of the diffusion constant is the same for the two.

In an aerogel with a finite fractal range, Λ' is a multiple of the mean pore size, so the upper limit of the permeability behaves as

$$K \propto (c_{crit}-c)(c_{crit}-c)^{(-2D_f+5)/3} \tag{14}$$

where c is the concentration of the aerogel at a given stage of densification.

We recall that the permeability is the product of the accessible porous volume and the ratio $\langle r^2\rangle/\Lambda'$. In this case, an easy calculation gives an upper limit to the critical exponent which is equal to $1 + (5-2D_f)/3 = 1.4667$ (for $D_f = 1.8$).

2.4. Closing pores; the mean-field approach

Another interesting point is the critical behaviour of the pore size near the percolation transition. Here again we shall use a mean-field approximation.

As seen before, the mean accessible pore size, here called ξ, may be estimated from

$$\xi \propto (c_{crit}-c)^{1/3} \tag{15}$$

where c is the concentration (density) of the aerogel (densified). Once again we take ϵ as a small difference, $\epsilon = c_{crit} - c$. An easy calculation gives a critical exponent for the pore size near the percolation transition of $\alpha = 1/3$. So the pore mean size tends to the critical pore mean size at the percolation transition: above it (for $c < c_{crit}$) the pore network is infinite and, when approaching the percolation transition, all of the open pores close and get a finite size.

3. Results and discussion

The computations for the aerogel were carried out by applying a diffusion-limited cluster–cluster aggregation method to a cubic lattice [4,5]. This method is known to represent aerogels which have a fractal dimension $D_f = 1.8$. The aerogel was built in a cubic box with periodic boundary conditions. The cubic box has an edge length equal to $100a_0$ (where a_0 is the edge length of one particle before densification). The aerogel initial concentration was taken as equal to 0.05.

We used the same numerical procedure as in reference [6]: a gas particle is released at random inside a pore of the aerogel and then is allowed to have a ballistic motion between the pore walls. At each collision with the pore walls, the Knudsen law [9] is used to randomly choose a new direction for the gas particle motion. At the end of the process, for a given number of collisions, the total length of the trajectory Λ and the end-to-end square displacement $\langle r^2\rangle$ are computed. The diffusion constant is then deduced from the formula $D = \langle r^2\rangle/\Lambda$.

We built 60 different numerical aerogels. For each geometrical configuration of the numerical DLCA aerogel, we took an average over 100 different realizations of the diffusion process. The resulting permeability is hence an average over 6000 diffusion paths of the gas particle.

In figure 1, we have plotted the permeability as a function of $c_{crit} - c$. The critical concentration has been calculated by means of formula (2). Here $c_p = 0.3117$ is the percolation

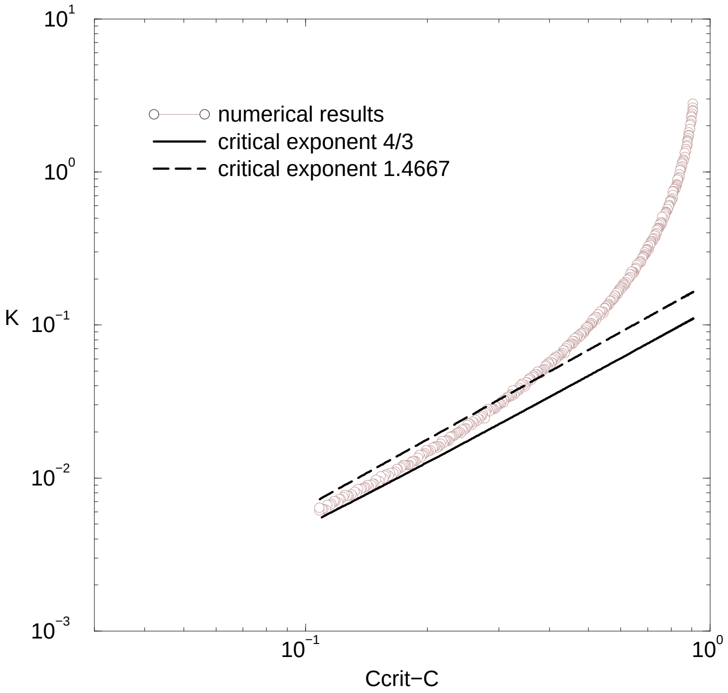

Figure 1. A log–log plot of the behaviour of the critical permeability K as a function of $c_{crit} - c$ for sintered aerogels, computed numerically. The circles represent the numerical behaviour, the solid line represents the theoretical mean-field behaviour with a predicted exponent of 4/3 and the dashed line represents the theoretical behaviour with a predicted exponent of 1.4667. In this case, numerical samples have an initial density $c_0 = 0.05$ and the percolation critical density is $c_{crit} = 0.96$.

threshold for a cubic lattice [10] and c is the aerogel density. In the particular case of figure 1, the initial density of the densifying aerogel was $c_0 = 0.05$, so the percolation threshold was found with formula (1) to be approximately $c_{crit} = 0.96$. The solid line represents the theoretical critical behaviour $(c_{crit} - c)^{\kappa_p}$ with $\kappa_p = 4/3$, in the mean-field approximation, and the long-dashed line represents the theoretical behaviour of the permeability for the upper limit of the critical exponent 1.4667. As one can see, the behaviour of the numerical results is located between $K \propto \epsilon^{4/3}$ and $K \propto \epsilon^{1.4667}$.

The critical exponent for the permeability of gases through aerogel lies between two values: 4/3 and 1.4667. The upper limit of this critical exponent is given by a calculation which takes into account the fractal character of this type of material. But, as the aerogels built with a diffusion-limited cluster–cluster aggregation method with periodic boundary conditions have a fractal domain which is finite, the permeability is also affected by the random distribution of the fractal clusters which compose the numerical aerogel (i.e. the DLCA aggregate with periodic boundary conditions).

A mean-field approach which leads to the critical exponent 4/3 only takes account of the mean pore distribution.

Anyway, the critical exponent for the permeability as a function of the density of the aerogel sample lies between $4/3$ and $1 + (5 - 2(1.8))/3 = 1.4667$. So this differs from the permeability behaviour in materials such as rocks. Indeed, in this type of random material, the critical exponent is equal to 2.0 [11].

4. Conclusions

In conclusion, we have calculated the permeability critical exponent near the percolation threshold. This exponent differs from those found for random media such as rocks. The fractal character of the aerogel structure induces different behaviours for the permeability and the gas diffusion constant. The behaviour depends on the fractal dimension of the sample in which the gas diffuses. The fractal character of the aerogel is the cause of the different behaviour of the diffusion constant.

Acknowledgments

Numerical calculations were performed on the computers of the CNUSC (Centre National Universitaire Sud de Calcul). We would like to acknowledge financial support from the CONICIT-CNRS project.

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