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Review

Influence of the Total Porosity on the Properties of Sintered Materials—A Review

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Abstract: Porosity is a characteristic present in most sintered materials, full densification only being achieved in special cases. For some sintered materials, porosity is indeed a desired characteristic, serving for the intended application of the material. In any case, the porosity present in materials can have a strong effect on some of their properties, both structural and functional. In this paper, some of the expressions proposed to describe the influence of the total porosity on the effective properties of sintered materials are examined. Moreover, a universal expression (with two fitting parameters) valid to satisfactorily represent all the analysed behaviours is proposed. One of these parameters can be assimilated to the tap porosity of the powders used to manufacture the material. The properties examined were elastic moduli, ultimate strength, thermal and electrical conductivities, magnetic characteristics, and other properties directly related to these ones. The study is valid for sintered materials, both metallic and ceramic, with a homogeneous and non-texturised microstructure.

Keywords: effective properties; porous materials; sintered materials; modelling; porosity influence

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1. Introduction

The properties of fully dense materials are defined by their chemical composition, the microstructure (on the atomic, nanometric and micrometric scales) and the microgeometry of the surface. On the other hand, the properties of materials not attaining full densification usually also depend on their porosity and, if these materials are obtained from powders, on the goodness of the junction between particles (the sintering quality).

However, this is not the case for all properties. In porous materials, including sintered ones, some properties show a decisive dependence on microstructural features, such as the crystalline structure, being much less sensitive to other microstructural features, such as the presence of porosity [1]. Thus, properties such as the specific heat capacity or the temperatures at which the phase transformations take place may appear to be almost insensitive to porosity. Pores, however, have a marked influence on the response to applied mechanical stresses, to the passage of an electric current, to the flow of heat, to the action of a magnetic field, etc. For other properties, such as the coefficient of thermal expansion, there is not a clear consensus regarding the dependence on the porosity. For sintered metallic materials [2], the coefficient of thermal expansion seems to be virtually independent of the porosity, but this does not seem to be the case for ceramic materials [3].

The effect of the presence of porosity can be modelled to make appropriate predictions on the material properties. Regarding sintered materials, the basic idea of considering two phases (pores + fully dense material) and a rule of mixtures may be an acceptable starting point. Any model based on this premise should include the property of the bulk (porosity-free) material and the porosity level of the compact. However, a refined model should also include microstructural parameters, such as the shape and size of the pores and maybe of the initial powder particles. Many attempts have been made in this direction [4–11]. Unfortunately, the variability of the morphological and dimensional characteristics of the porosity, together with the non-negligible effects of both the impurities usually present in commercial powders, and of the variable quality of the junctions between the powder particles, limits the applicability of the theoretical models. The difficulty in finding suitable values for these parameters means that, from a practical point of view, it is preferable to use empirical laws, with some fitting parameters inferred from experimental data, which often manage to provide very reasonable predictions. These are the models that are of greater interest to this work.

For almost completely dense materials, with only a low residual porosity, it can be assumed with reasonable accuracy that the relationship between the property and the porosity is linear. However, for higher porosities, most studies clearly show non-linear correlations. It is therefore expected that the presence of porosity leads to complicated laws, far from simple direct or inverse linear proportionality.

Many proposed models verify that the normalised or relative property with respect to that of the bulk material decreases from 1 to 0 (or increases from 1 to infinity) as the porosity varies from 0 to 1. These porosity limits represent a hypothetical and unreal situation, valid for a material whose porosity should vary from a merely residual value to that typical of a foam [12]. However, they are not at all acceptable when the materials retain microstructural details that clearly show their powdered origin. It cannot then be considered that the upper limit of porosity is 1, and it is more convenient to consider a value close to the so-called tap porosity (that of a powder mass in a state of equilibrium reached by moderate vibration [13]).

Regarding metallic materials, if the compact or porous aggregate has not been sintered, the problem becomes more complicated, as the solid phase may not be perfectly continuous. This is the case for compacts or aggregates obtained only by compacting powders, without the subsequent sintering step, which should complete the process. The metal particles that constitute the powder are coated with native oxides, which have a great influence (even more than the porosity itself) on the apparent value of certain properties, such as the electrical resistivity. Without the sintering process, which removes these barriers at the interparticle necks, there will be no continuity of the metallic phase throughout the material. However, in this work, the study of these cases will not be addressed.

The aim of this work is to gather some of the models proposed for the description of the mechanical, electrical, thermal, and magnetic properties of porous materials obtained from sintered powder particles. Since the existing references in literature are rather inhomogeneous, in terms of porosity or density, an attempt has been made to bring them together in a systematic way, to contribute to a more reliable characterisation of materials obtained from powders. It is intended to show that models for a particular property can also be valid, in a first approach, for other properties.

It is possible to find works in the bibliography dealing with the different expressions for certain properties (i.e., elastic and other mechanical properties, electrical and thermal conductivities, or magnetic properties), but models are not compared for different families of properties, and this is the main contribution of this work.

The second purpose of this paper is to show that there is a model that can be considered universal to correctly describe the porosity dependence of the studied properties, with the form described by Equation (1). This model can be considered an empirical equation, but there are also proofs in the field of percolation that lead to similar expressions for some of the properties discussed here.

$$p = p_0(1 - \Theta/\Theta_M)^n \tag{1}$$

where p is the property of the material with porosity Θ, p_0 is the property for the pore-free material, Θ_M is the maximum porosity of the powder mass, and n is a fitting parameter (positive or negative). Note that, considering a positive value for n, Equation (1) satisfies the expected boundary conditions, $p \to p_0$ as $\Theta \to 0$, and $p \to 0$ as $\Theta \to \Theta_M$, since, in this last situation, interparticle contacts are points. This is the case with most properties analysed in this paper, including Young's modulus, the electrical and thermal conductivities, etc. If n is a negative number, then $p \to p_0$ as $\Theta \to 0$, and $p \to \infty$ as $\Theta \to \Theta_M$, being the typical situation for properties such as the electrical or thermal resistivities or the magnetic coercivity. As later shown, Equation (1) has been previously proposed in various contexts and by different authors. The value of the maximum porosity Θ_M can be approximated for sintered materials by the so-called tap porosity, which is obtained by a moderate vibration of the starting powders [13].

For low porosities (i.e., when $\Theta \to 0$), Equation (1) can be approximated by Taylor expansion to:

$$p \approx p_0(1 - n\Theta/\Theta_M) = p_0(1 - a\Theta) \tag{2}$$

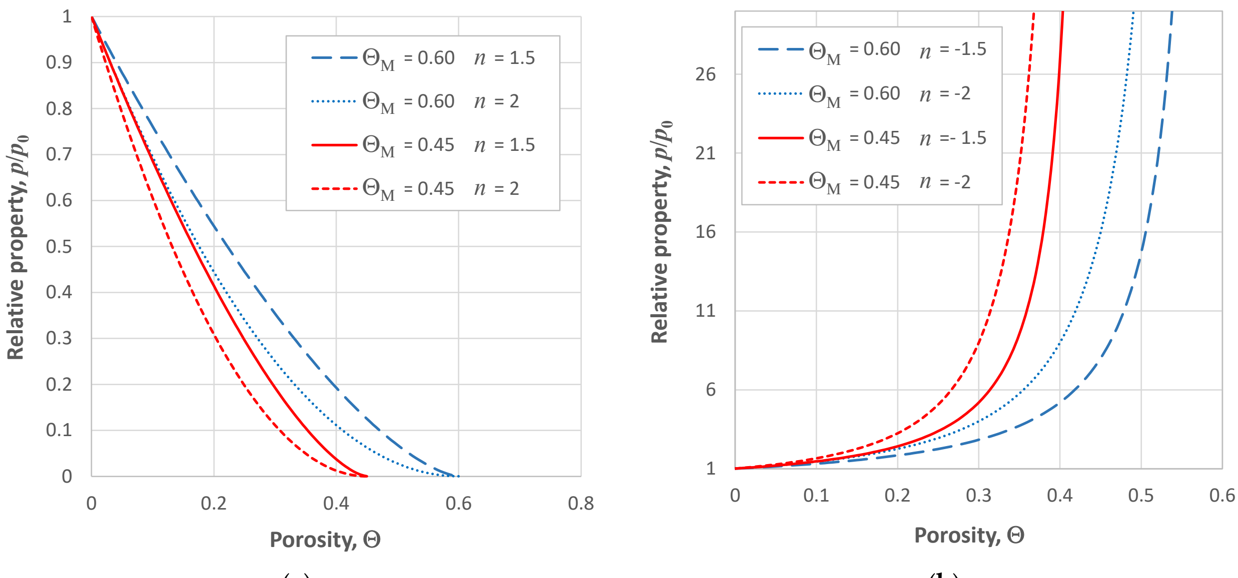
which describes a linear behaviour, often observed and proposed for sintered materials with low residual porosity.

Finally, it can be said that Equation (1) is a generalisation of Archie's law [14] (which originally was presented to relate the in situ electrical conductivity of a porous rock to its porosity):

$$p = p_0(1 - \Theta)^n \tag{3}$$

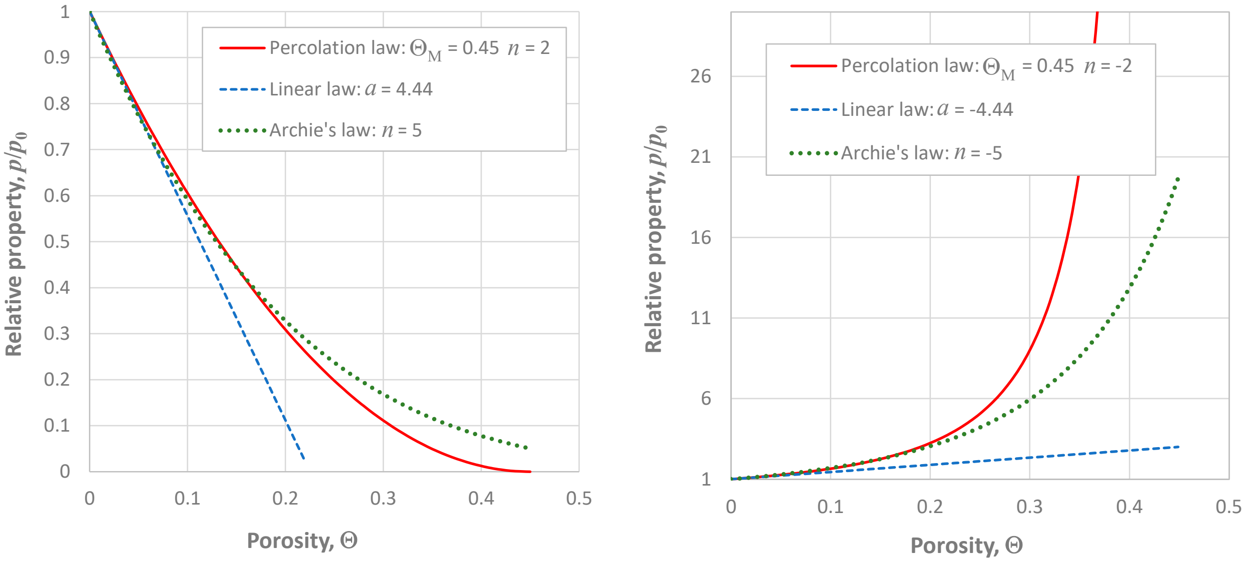
Relatively recent studies on porous materials [15–17] suggest that Equation (3) is well suited to describe the porosity dependence of various properties such as mechanical, thermal, and electrical ones. Nevertheless, Equation (1) is a generalisation more consistent with the physical limits expected in the range of porosity of sintered materials.

Figure 1 shows the characteristics and differences among the aforementioned equations. The variation with the porosity of the property p normalised by p_0 (i.e., relative property, p/p_0), given by the percolation law expressed by Equation (1), is plotted for some of the values of the parameters Θ_M and n in Figure 1a,b. In Figure 1c,d, one of the previous curves is again represented together with the linear approximation given by Equation (2) and Archie's law given by Equation (3). As can be seen, Equation (2) and Equation (3) are, for low porosities, very close to Equation (1), which gives an idea of the difficulty in deciding which theoretical model should be adopted to better represent the trend of experimental data. However, the superiority of Equation (1) lies in the compliance of the expected lower and upper physical limits, suitable for sintered materials.



(**a**) (**b**)

Figure 1. *Cont.*



(**c**) (**d**)

Figure 1. Dependence on the porosity of the normalised property p/p_0: (**a**) according to Equation (1) for different values of Θ_M and positive n; (**b**) *idem* with negative n; (**c**) comparison for the models given by Equations (1)–(3) for positive values of n; (**d**) *idem* for negative n.

The interest in formulating analytical expressions relating properties with the porosity level comes from a long time ago. Because of computational advances, a big effort in developing analyses based on finite or discrete elements is nowadays found. The actual trend goes in the direction of computing (by FEM, DEM, etc.) the property of a virtually recreated material, based on detailed features such as the mean pores size, the size distribution, pore connectivity, roundness, axiality, etc. This allows one to know the influence of such detailed features on the studied property, testing multiple variants.

Nevertheless, knowing these microstructural features from the processing conditions is usually a problem even more difficult than the original problem regarding the studied property. Thus, these models are at times only slightly predictive, because of the need for detail and complexity to obtain microstructural information (usually through destructive tests). Obtaining this information is also much more complex than the measurement of the total porosity of the specimen, or the tap porosity of the starting powder. Thus, despite the detailed analysis of the porosity is an actual trend that must be explored, its applicability from a practical point of view is uncertain.

However, the use of relatively simple expressions relating properties and porosity allows for both obtaining quick estimations and easily understanding the sensitivity of certain parameters. Moreover, it allows for finding analogies among apparently disconnected properties. It should also be considered that, in some cases, the computing effort with modern techniques does not always lead to better estimations. Simpler analytical models can be more easily applied, although it would be desirable to deepen the theoretical study to find the physical meaning of the involved parameters, mainly of the exponents, which should be estimated theoretically or from simple tests.

In the following sections, experimental data covering the wider range of porosity have been selected. This allows for a better evaluation of the goodness of the different proposed expressions when fitting models to data.

2. Influence of Porosity on Elastic Properties

Knowledge of materials' elastic properties is critical in the design of structural applications. Accordingly, their dependence on porosity has received early attention from researchers. A typical critical application is that of porous metallic implants for medical applications, which are generally obtained by powder metallurgy techniques. The high mismatch between the Young's moduli of the bone (10–30 GPa) and the metallic implant (105–110 GPa for titanium and its alloys) can damage the bone tissue adjacent to the implant, shortening the efficiency and lifetime of the orthopaedic solution [18]. This problem can be alleviated by reducing the Young's modulus of the implant material by introducing porosity into the implant. The optimisation of this solution requires perfect knowledge of the relationship between the Young's modulus and the porosity of the porous material. The sought relationship will be of the type:

$$E = E_0 \cdot f(\Theta; \{c_i\}) \tag{4}$$

where E is the Young's modulus of the porous material, E_0 is the Young's modulus of the solid (pore-free) material, and $f\,(\,)$ is a function of Θ and $\{c_i\}$, a set of empirical or fitting parameters sensitive to the microstructural details of the material.

It was probably Dewey [19] who first proposed a linear relationship valid for low porosities. Naturally, more sophisticated expressions followed [20–34]. Table 1 shows some of the different equations proposed for the Young's modulus of any porous material normalised by that of the completely solid (pore-free) material. Equations have been classified into four categories: linear, power, exponential and other equations. A more detailed study, including the different authors who have experimentally tested each one of the equations, can be found in [35].

Table 1. Summary of equations for the relative Young's modulus of porous materials ($E_R = E/E_0$). Θ_{M} is the maximum porosity of the powder mass. Parameters c_1 to c_{17} are fitting constants.

E_R Equation Form	Researcher	Year	$E_R \to 1$ if …	$E_R \to 0$ if …
		Linear equations		
$1 - c_1\Theta$	Dewey [19]	1947	$\Theta \to 0$	$\Theta \to {c_1}^{-1}$
		Power equations		
$(1-\Theta)^{c_2}$	Bal'shin [20]	1949	$\Theta \to 0$	$\Theta \to 1$
$\left(1 - c_3\Theta + c_4\Theta^2\right)$	Mackenzie [21]	1950	$\Theta \to 0$	Solution of quadratic equation
$(1 - c_5\Theta)^{c_6}$	McAdam [22]	1951	$\Theta \to 0$	$\Theta \to {c_5}^{-1}$
$\left(1-\Theta^{\frac{2}{3}}\right)/\left(1-\Theta^{\frac{2}{3}}+\Theta\right)$	Paul [23]	1960	$\Theta \to 0$	$\Theta \to 1$
$1 - c_7\Theta^{\frac{2}{3}}$	Eudier [24]	1962	$\Theta \to 0$	$\Theta \to {c_7}^{-\frac{3}{2}}$
$[1-(\Theta/\Theta_{\mathrm{M}})]^{c_8\Theta_{\mathrm{M}}}$	Bert [25]	1985	$\Theta \to 0$	$\Theta \to \Theta_{\mathrm{M}}$
$\left(1-\Theta^{\frac{2}{3}}\right)^{c_9}$	Boccaccini and Fan [26]	1997	$\Theta \to 0$	$\Theta \to 1$
$[1-(\Theta/\Theta_{\mathrm{M}})]^{c_{10}}$	Roberts and Garboczi [27]	2000	$\Theta \to 0$	$\Theta \to \Theta_{\mathrm{M}}$
		Exponential equations		
$\exp(-c_{11}\Theta)$	Ryshkewitch [28]	1953	$\Theta \to 0$	$\Theta \to 1$ with $c_{11} \gg 1$
$1 - \exp(-c_{12}(1-\Theta))$	Rice [29]	1976	$\Theta \to 0$ with $c_{12} \gg 1$	$\Theta \to 1$
$\exp\left(-c_{13}\Theta - c_{14}\Theta^2\right)$	Wang [30,31]	1984	$\Theta \to 0$	$\Theta \to 1$ with $c_{13} \gg 1$ and/or $c_{14} \gg 1$
		Other equations		
$(1-\Theta)/(1+c_{15}\Theta)$	Hashin [32]	1962	$\Theta \to 0$	$\Theta \to 1$
$1 + (c_{16}\Theta)/(1 - c_{16}\Theta - \Theta)$	Hasselman [33]	1962	$\Theta \to 0$	$\Theta \to 1$
$(1-\Theta)^2/(1+c_{17}\Theta)$	Ramakrishnan and Arunachalam [34]	1990	$\Theta \to 0$	$\Theta \to 1$

Examination of Table 1 allows for selecting those expressions with realistic boundary conditions to be properly applied to sintered materials, that is: $E_R \to 1$ for $\Theta \to 0$, and $E_R \to 0$ for $\Theta \to c$, where $c < 1$. The constant c acts as a maximum or threshold porosity (for instance, the tap porosity). The only expressions that could satisfy these bounds are those proposed by Dewey, McAdam and Eudier (considering values higher than 1 for the constants c_1, c_3 and c_7), as well as those by Bert and Roberts-Garboczi. Other equations can also satisfy these limits, but constants must satisfy certain conditions, therefore not being free fitting parameters.

The expressions by McAdam, Bert, and Roberts-Garboczi are essentially equivalent to the percolation law represented by Equation (1). McAdam derived his equation after the statistical processing of a large amount of experimental data, obtained using ultrasonic measurements. Bert, on the other hand, proposed his expression on the basis of previous theoretical studies. Roberts and Garboczi criticised some theoretical attempts to derive expressions from microstructural features and characteristics, opting for an empirical solution, consistent with the expected physical limits. The equation by Dewey is of the linear type represented by Equation (2). The Bal'shin equation, of the Archie type represented by Equation (3), is a particular case of the percolation law and, although it is still widely used, its upper limit of porosity is 1, an unrealistic value for sintered materials. Other researchers who have successfully tested the same power law are Phani et al. [36–40], Wagh et al. [41], and Maitra and Phani [42]. It can be concluded from these studies that the parameters c_3 and c_4 in the McAdam-type expression take values between 1 and 4, and between 2 and 4, respectively. According to the value of c_3, the value of Θ_M in the equivalent Equation (1) should be about 0.4, an acceptable value for the tap porosity. In Roberts-Garboczi's expression, the parameter c_{10} moves between 1 and 3, with typical values of Θ_M between 0.35 and 0.65. For the Bal'shin expression, if $\Theta < 0.5$, the constant $c_2 \approx 3.4$ [43]. According to this, it could be considered that the value of n in Equation (1) should be between 1 and 4 to properly represent the behaviour of the Young's modulus.

Experimental data obtained with reduced iron powder pressed between 49 and 882 MPa and sintered at 1200 °C [44] have been fitted, by the least squares method, with the linear law (Dewey), power-type Archie's law (Bal'shin), percolation law, Eudier's law, Ryshkewitch's law and Wang's law, as shown in Figure 2. The considered value for E_0, obtained from the original data, has been 225 GPa. Other equations in Table 1 are not represented in Figure 2 because of not satisfying the limit conditions expected for sintered materials.

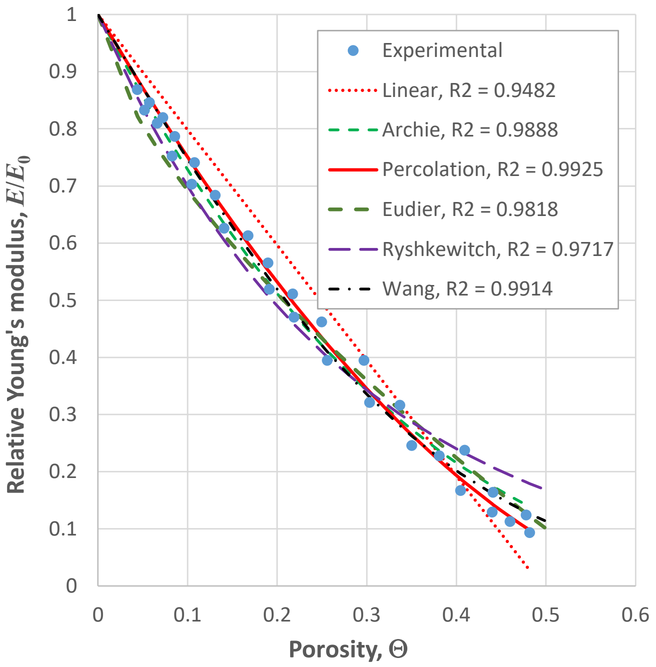


Figure 2. Experimental values of relative Young's modulus vs. porosity [44] and fitting with the linear law (Dewye), Archie's law (Bal'shin), percolation law, Eudier's law, Ryshkewitch's law and Wang's law.

Despite the fitting being good with all equations, a higher coefficient of determination (R^2) of 0.99 is attained with the percolation law, with a realistic value for Θ_M of 0.65 and a value for n of 1.72. This value of n is in the expected range according to the studies of the percolation law above commented. A high determination coefficient is also attained with the Wang's law because of having two fitting parameters.

To model the porosity dependence of the shear modulus, G, similar expressions to those for Young's modulus have usually been proposed, with the proper values of the involved parameter. Thus, Kováčik [45–47] assumed an equation similar to the percolation law to describe the porosity dependence of the Young's and shear modulus in porous materials. Naturally, the parameter Θ_M (the maximum porosity of the system) must be identical in both cases (as it can be interpreted as a percolation threshold). However, the characteristic exponents of the Young's and shear modulus need not be identical, in general. Thus, assuming that Young's modulus is described by:

$$E = E_0[1 - (\Theta/\Theta_M)]^{n_E} \tag{5}$$

and the shear modulus by:

$$G = G_0[1 - (\Theta/\Theta_M)]^{n_G} \tag{6}$$

and taking into account that for homogeneous isotropic materials the Poisson's ratio v can be determined from the moduli E and G as follows:

$$v = \frac{E}{2G} - 1 \tag{7}$$

substituting Equations (5) and (6) in Equation (7) produces the following:

$$v + 1 = (v_0 + 1)[1 - (\Theta/\Theta_M)]^{n_E - n_G} \tag{8}$$

In the particular case that $n_E = n_G$ or $n_E \approx n_G$, then $v = v_0$ or $v \approx v_0$, which justifies experimental results [47] indicating a certain insensitivity of the Poisson's ratio with respect to the porosity, for not very high values of porosity. In practice, a difference of $n_E - n_G = 0.09$ is reported in [47] for sintered iron studied in the porosity range from 0 to 0.22. The model is also able to describe negative values of the Poisson's ratio of porous materials when approaching the maximum value of the porosity, Θ_M (percolation threshold).

3. Influence of Porosity on Ultimate Strength

Mechanical properties, and especially ultimate strength, are of great importance for many sintered materials, serving as indicators to assess and optimise the sintering processes. This justifies the studies to relate mechanical properties and material porosity. A study of porous sintered metals [48] shows that the most important factor influencing mechanical properties is the pore content. Powder characteristics, such as pore size, particle shape and distribution, sintering atmosphere, temperature and time, have lesser effects. Nevertheless, many studies with this same objective are developed in a different field, such as the resistance study of rocks containing pores. In this later field, studies are mainly directed to assess the compressive strength. There is, however, no reason to evaluate the expressions developed both for tensile and compressive conditions in a conjunction mode.

Pores reduce the effective cross-section of parts, negatively affecting their mechanical strength. Therefore, porosity reduction is an obvious objective to achieve a high ultimate strength and, in general, good mechanical properties. For low residual porosities, strength may have a complex dependence on pore structure and particle boundaries. For high porosities, the size and quality of the sintering necks between particles clearly determines the mechanical strength of the material.

Different models have been suggested for the ultimate strength dependence with the particle neck size and/or porosity of sintered materials [49]. A complete review can be found in [50]. The sought relationships should be of the form:

$$\sigma_U = \sigma_{U0} \cdot f(\Theta; \{c_i\}) \tag{9}$$

where σ_U is the ultimate tensile strength of the porous material, σ_{U0} is the same property referred to the solid material (free of porosity) and f ( ) is a function of the porosity Θ and of $\{c_i\}$, a set of empirical or fitting parameters, which vary with the pore structure, the bonding degree between particles, etc.

Table 2 shows some of the different equations, both of power and exponential type, proposed for the ultimate strength (tensile or compressive) of porous materials normalised by the corresponding value for the fully dense material. They all describe, as expected, the decrease in strength with increasing porosity.

Table 2. Summary of relationships for the relative ultimate strength of porous materials ($\sigma_{UR} = \sigma_U/\sigma_{U0}$). Parameters c_1 to c_5 are fitting constants.

σ_{UR} **Equation Form**	**Researcher**	**Year**	$\sigma_{UR} \to$ **1 if . . .**	$\sigma_{UR} \to$ **0 if . . .**
$(1-\Theta)^{c_1}$	Bal'shin [20]	1949	$\Theta \to 0$	$\Theta \to 1$
$\exp(-c_2\Theta)$	Ryshkewitch [28]	1953	$\Theta \to 0$	$\Theta \to 1$ with $c_2 \gg 1$
$(1-\Theta)/(1+c_3\Theta)$	Hashin [32]	1962	$\Theta \to 0$	$\Theta \to 1$
$1 - c_4\Theta^{\frac{2}{3}}$	Eudier [51]	1968	$\Theta \to 0$	$\Theta \to {c_4}^{-\frac{3}{2}}$
$(1-c_5\Theta)^2$	Rzhevsky and Novik [52]	1971	$\Theta \to 0$	$\Theta \to {c_5}^{-1}$

One of the first proposed expressions is the Archie-type law due to Bal'shin [20], who found that the value of the parameter c_1 ranged from 3 to 6, for metallic and ceramic materials. A few years later, studying sintered pure alumina and partly magnesia-stabilised zirconia under compression, Ryshkewitch [28] proposed an exponential expression in which the constant c_2 took a value close to 4.3. The equations by Hashin [32] and Eudier [51] were already proposed in the context of elastic properties. As then stated, the Eudier's equation reaches the upper bound for a porosity lower than 1. In particular, Eudier found a value of c_4 = 1.21, which leads to a maximum porosity of 0.75. A new power law was years later proposed by Rzhevsky and Novik [52]. Haynes et al. [53] tested in detail the Hashin's equation [32] with steel specimens, concluding that certain modifications related to the pore stress concentration factor were necessary for a better fitting to experimental data. Salak et al. [54,55] analysed the relationship with porosity of the tensile strength, elongation and hardness of sintered iron compacts, on the basis of a large number of tests and previously proposed equations.

Some of the expressions gathered in Table 2 coincide with those proposed (sometimes by different authors) for the Young's modulus (Table 1). It is surprising, however, that the porosity dependence of the ultimate strength has received less attention from researchers, who could have used the theoretical effort already made for the elastic properties. It is especially surprising that a percolation law similar to Equation (1) has not been proposed in this context. However, the power law expression by Rzhevsky and Novik is a particular case of the percolation law with $c_5 = 1/\Theta_M$ and the exponent n = 2.

Regarding the applicability of these expressions to sintered materials, only the one by Rzhevsky and Novik, the one by Eudier and the exponential one can fulfil the bounds of sintered materials. Figure 3 shows the fitting of the linear law, Archie's law (Bal'shin), percolation law, Ryshkewitch's law, Eudier's law and Rzhevsky-Novik's law to the data obtained for Cu compacts under a sintering temperature near 1015 °C [56]. The ultimate strength of the pore-free material has been fixed at 321 MPa, according to extrapolations from the original work. This time, the linear law is clearly worse than others. The best fit is obtained with the percolation law, with a coefficient of determination (R^2) of 0.95, with a realistic value for Θ_M of 0.51 and a value of n of 2.5. The results obtained with the equation by Rzhevsky and Novik are very similar, even with the exponent having a fixed value, being obtained a realistic Θ_M value of 0.44 from c_3.

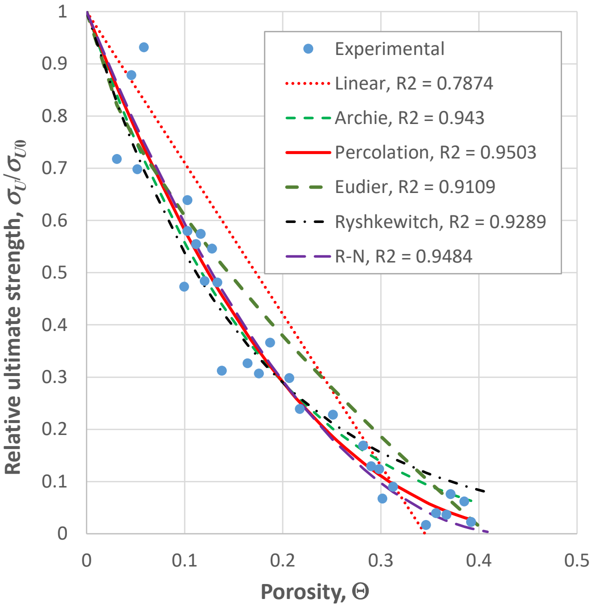


Figure 3. Experimental values of the relative ultimate strength vs. porosity [56], and fitting with the linear law, Archie's law (Bal'shin), percolation law, Ryshkewitch's law, Eudier's law and Rzhevsky-Novik's law.

Similar equations to those proposed for the ultimate strength could be, a priori, proposed for the yield strength [7]. However, the strengthening mechanisms induced by alloying elements seem to be phenomena coupled with the presence of porosity, making it difficult to propose general behaviour laws as a function of the porosity [43].

A mechanical property strongly correlated with ultimate strength is indentation hardness. The presence of porosity makes it necessary to differentiate between true hardness (or microhardness) and apparent hardness. The true hardness can be determined in a porous sintered material by indenting a single powder particle of the material using very low loads. Obviously, the hardness of a single powder particle of sintered material depends only on the local composition and the microstructural state, and it will therefore not differ from the hardness of the analogous fully dense material. The apparent hardness, on the other hand, is the result of measurements made with higher loads, including the effect of porosity.

To describe the porosity dependence of the apparent hardness, similar expressions to those given in Table 2 for the ultimate strength could be used. However, often, the strong scatter of the results made several authors propose purely linear correlations, although they are clearly not linear [1,57,58].

The applicability of these expressions to study the relative hardness of sintered materials is analysed in Figure 4. The fitting of the linear law, Archie's law (Bal'shin), percolation law, Ryshkewitch's law, Eudier's law and Rzhevsky-Novik's law to the Vickers hardness data obtained for 3Y-TZP (3 mol% yttria-stabilised tetragonal zirconia polycrystal) is studied. Specimens were prepared by die pressing followed by cold isostatic pressing, subsequently sintered at temperatures in the range 1150–1450 °C [59]. The microhardness of the 3Y-TZP has been fixed in 11 GPa, according to extrapolations from the original work. Again, compared to other laws, the linear law is the worst. The percolation law reaches a coefficient of determination (R^2) of 0.99, with a value for Θ_M of 0.72 and a value for n of 2.6. The other power or exponential laws also reach high correlation coefficients.

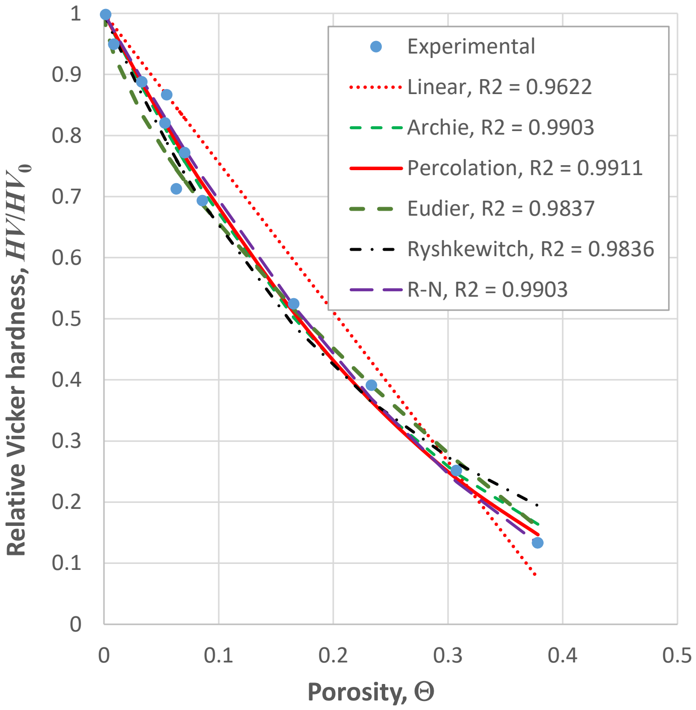


Figure 4. Experimental values of relative Vickers hardness vs. porosity [59], and fitting with the linear law, Archie's law (Bal'shin), percolation law, Ryshkewitch's law, Eudier's law and Rzhevsky-Novik's law.

Other mechanical properties, such as impact strength, fracture toughness and fatigue strength are also sensitive to the presence of porosity and microstructure [60,61]. For high porosity, the relationships for fatigue behaviour are clearly non-linear [1,57]. For low porosities, the behaviour depends on the microstructure, including pore size and spacing. When the plastic zone in front of an advancing crack is close to the pore size, the pores cannot prevent fatigue crack propagation and rapid failure occurs. In such situations, for the correct description of the material behaviour, it is not enough to know the level of porosity, but information about the microstructure is required. This means that the adjustable empirical parameters will be exposed to high variability [62].

4. Influence of Porosity on Thermal and Electrical Conductivities

Moving to other properties, outside the mechanical behaviour, it is noteworthy to consider the electrical and thermal properties. The correct knowledge of the influence of porosity on the conductivity of pieces acting as electrical contactors or thermal dissipators is crucial to optimise their performance. In addition, the influence of porosity is of interest because there are powder manufacturing processes that are highly influenced by the presence of porosity. For example, sintering processes based on the passage of electricity through the powder mass and the generated Joule heating, such as spark plasma sintering or electrical resistance sintering, need to know the porosity influence. Moreover, the electrical conductivity is an extremely sensitive property that can be measured with a high accuracy, and, therefore, it has usually been used to assess the sintering degree.

The thermal and electrical conductivities of sintered materials are reduced by the presence of pores (or other non-conductive inclusions). In general, the effective conductivity decreases as the porosity increases. This is true for the electrical conductivity, since the gaseous phase filling the pores has zero electrical conductivity, but also for thermal conductivity, since the conductivity of gases is very low. Moreover, heat transmission by radiation should be considered at high temperatures but does not affect the electric conduction. Nevertheless, these differences are negligible in most situations, and can be ignored in practice.

The sought relationship is again of a similar form:

$$g = g_0 \cdot f(\Theta; \{c_i\}) \tag{10}$$

where g is the thermal or the electrical conductivity of the porous sintered material, g_0 is the same conductivity of the fully dense material and f ( ) is a function of Θ and $\{c_i\}$, a set of empirical or fitting parameters sensitive to the microstructural details of the material. Since the models are used interchangeably in thermal or electrical contexts, regardless of the original context, we will consider them equally valid for both problems (electrical and thermal problems). This idea is clear for metallic materials, with electrons being the main carriers for the electric current and the heat. For ceramic materials, with different carriers to transport electric current and heat (electrons and phonons, respectively), the previous idea can be valid if pores have a micrometric size, much greater than the typical atomic size controlling the scattering phenomena.

Unfortunately, porosity is often less important than the presence of impurities in determining conductivity, despite the fact that the effect of impurities disappears with higher temperature while that of the pores remains, as shown in [2] for porous sintered steels. Therefore, to validate models, special care has to be taken to avoid any contamination during the sintering process. It has also been checked that for low porosities, the electrical conductivity of sintered metallic materials follows the same behaviour as the thermal conductivity. For high porosities and high temperatures, however, the relationship between thermal and electrical conductivity is sensitive to the microstructure. The lower the intrinsic conductivity of the material, the higher this structural sensitivity.

In fact, conductivity must decrease with porosity. The lower the porosity, the larger the transfer cross-section of the flux and the shorter the path it must travel, avoiding the pores. Many models were proposed a long time ago. Table 3 gathers some of those models.

Table 3. Different expressions for the relative conductivity (electrical or thermal) of porous materials ($g_R = g/g_0$) as a function of the compact porosity (Θ). Θ_{M} is the maximum porosity of the powder mass, and the remainder parameters c_1 to c_7 are fitting constants.

g_R **Equation Form**	**Researcher**	**Year**	$g_R \to$ **1 if . . .**	$g_R \to$ **0 if . . .**
$\frac{2(1-\Theta)}{2+\Theta}$	Maxwell [63]	1873	$\Theta \to 0$	$\Theta \to 1$
$\frac{1-\Theta}{1+c_1\Theta}$	Fricke [64]	1924	$\Theta \to 0$	$\Theta \to 1$
$(1 - c_2\Theta)$	Loeb [65]	1954	$\Theta \to 0$	$\Theta \to 1/c_2$
$\left[3(1-\Theta)^{c_3} - 1\right]\left(\frac{1-\Theta}{2+\Theta}\right)$	Murabayashi et al. [66]	1969	$\Theta \to 0$	$\Theta \to 1$
$\frac{1-\Theta}{1+c_4\Theta^2}$	Aivazov and Domashnev [67]	1971	$\Theta \to 0$	$\Theta \to 1$
$\frac{c_5(1-\Theta)}{c_5+\Theta}$	Meyer [68]	1972	$\Theta \to 0$	$\Theta \to 1$
$(1-\Theta)^{c_6}$	Schulz [69]	1981	$\Theta \to 0$	$\Theta \to 1$
$(1-\Theta/\Theta_{\mathrm{M}})^{\frac{3}{2}\Theta_{\mathrm{M}}}$	McLachlan [70]	1986	$\Theta \to 0$	$\Theta \to \Theta_{\mathrm{M}}$
$(1-\Theta)^2(1-\Theta/\Theta_{\mathrm{M}})^{c_7}$	Gruzdev et al. [71]	1989	$\Theta \to 0$	$\Theta \to \Theta_{\mathrm{M}}$
$(1-\Theta/\Theta_{\mathrm{M}})^2$	Montes et al. [72]	2003	$\Theta \to 0$	$\Theta \to \Theta_{\mathrm{M}}$
$1 - \frac{3}{2}\Theta + \frac{1}{2}\Theta^2$	Pabst [73]	2005	$\Theta \to 0$	$\Theta \to 1$
$\left(1 - \frac{1}{2}\Theta\right)(1-\Theta/\Theta_{\mathrm{M}})$	Pabst and Gregorová [74]	2006	$\Theta \to 0$	$\Theta \to \Theta_{\mathrm{M}}$
$(1-\Theta)^{\frac{3}{2}}\left(1-(\Theta/\Theta_{\mathrm{M}})^{\frac{4}{3}}\right)^{\frac{1}{2}}$	Solonin and Chernyshev [75]	2006	$\Theta \to 0$	$\Theta \to \Theta_{\mathrm{M}}$

Table 3. *Cont.*

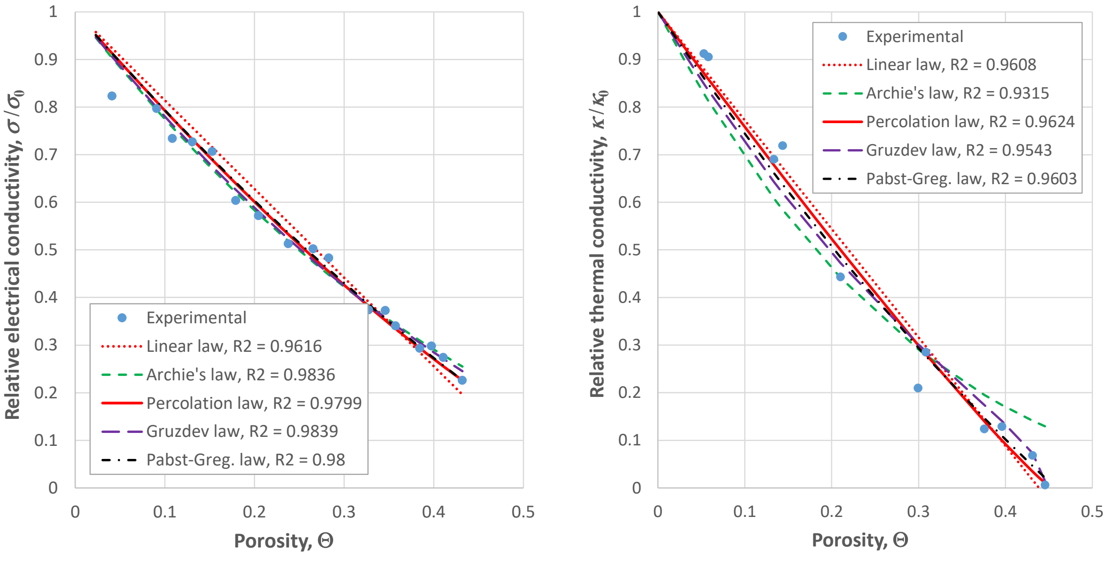
g_R **Equation Form**	**Researcher**	**Year**	$g_R \rightarrow 1$ **if . . .**	$g_R \rightarrow 0$ **if . . .**
$(1-\Theta/\Theta_M)^u$ $u = 1 + (1-\Theta_M)^{\frac{4}{5}}$	Montes et al. [76]	2008	$\Theta \rightarrow 0$	$\Theta \rightarrow \Theta_M$
$(1-\Theta/\Theta_M)^{\frac{3}{2}}$	Montes et al. [77,78]	2016–2018	$\Theta \rightarrow 0$	$\Theta \rightarrow \Theta_M$

As can be seen in Table 3, most expressions include an empirical parameter. Conductivity is closely dependent on the microstructure (including pore shape and pore size), and the empirical parameter helps to model the microstructural influence. Therefore, a simple mathematical expression based solely on the porosity level, as is the case for the Maxwell expression without any additional empirical parameter, can hardly describe the electrical conductivity for different porosities.

Most of the expressions in Table 3 verify that the relative conductivity decreases from 1 to 0 as the porosity varies from 0 to 1. However, these limits cannot be applied to powdered materials, since their maximum porosity is always much lower than 1. Only the expressions of Loeb [65], McLachlan [70], Gruzdev et al. [71], Pabst and Gregorová [74], Solonin and Chernyshev [75] and Montes et al. [72,76–78] take this upper limit of porosity into account, being therefore applicable in the high porosity range of powdered materials. In addition, the expressions of McLachlan [70] and Montes et al. [72,76–78] are specific cases of Equation (1).

In the Loeb expression, widely used in situations of low to medium porosities, the constant c_2 usually takes values between 1 and 2 [65].

Figure 5 analyses the applicability of these expressions to model the relative electrical and thermal conductivities of sintered materials. The fitting of the linear law, Archie's law, percolation law, Gruzdev's law and Pabst-Gregorová's law to the electrical conductivity measured for iron compacts, is studied in Figure 5a. Solonin-Chernyshev's law has not been included in Figure 5 because of resulting in slightly worse fitting than the other laws. Specimens were prepared by uniaxial cold compaction followed by 30 min of sintering in argon at 1150 °C [76]. Measurements were carried out at room temperature. The electrical conductivity of the fully dense material was 8.5×10^6 $(\Omega{\cdot}m)^{-1}$, and the experimentally measured tap porosity of the powder was 0.63.



(**a**) (**b**)

Figure 5. Experimental values of: (**a**) relative electrical conductivity vs. porosity for sintered iron powders [76]; (**b**) relative thermal conductivity vs. porosity for sintered alumina powders [79], and fitting with linear law, Archie's law, percolation law, Gruzdev's law and Pabst-Gregorová's law.

A high coefficient of determination (R^2) is attained with laws different to the linear. Nevertheless, not every proposed expression can be considered good just based on the value of R^2. For example, the expression by Gruzdev, with the higher coefficient, leads to a value of Θ_M of 0.57, which is far from the experimental value. Nevertheless, it is noteworthy that this expression does not have any free fitting parameter. The obtained values of Θ_M with the Pabst-Gregorová's and percolation laws are 0.61 and 0.67, respectively, both around the experimental value. It can be finally said that Pabst-Gregorová's law does not have free fitting parameters either, and the obtained value of n in the percolation law is 1.44. This value of n can now be compared with the exponents expected in the different percolation-type laws. Thus, the expected exponents range from 0.95 [70] to 2 [72], with the values of 1.45 [76] and 1.5 [77,78] providing better approximations.

The fitting of the same laws to the thermal case is shown in Figure 5b. Experimental data were measured for two types of alpha alumina compacts. Specimens were prepared by cold compaction and sintering [79]. The thermal conductivity of the fully dense material has been estimated in 36 $W \cdot m^{-1} \cdot K^{-1}$ [80].

A similar determination coefficient is attained with the used laws, even with the linear one. Moreover, the laws with the parameter Θ_M lead to a very similar value of about 0.45, a typical value for equiaxed powders. The value of n in the percolation law is 1.11. Thus, in order to attain this value, the expected Θ_M in the expression by McLachlan [70] and Montes el al. [76] are 0.74 and 0.94, respectively, both of which are far from the expected value of 0.45.

A final reflexion can be made regarding the similitude between the electrical and thermal conductivities. If the electrical and thermal conductivities of a given material are correctly described by Equation (1), it is obvious that the parameter Θ_M should be the same, but the exponent n would not necessarily coincide. If the exponents of the electrical and thermal conductivities were equal, the normalised thermal and electrical conductivities would be equal (i.e., $k_R = \sigma_R$). This seems to have been confirmed experimentally for sintered metallic materials in [72], in the low porosity range (0–0.25), but not for higher porosities. This means that, despite the fact that proposed equations can be applied to both the electrical and thermal cases, the fitting parameters for the electrical and thermal conductivities of a particular material do not necessarily have the same value. In the case of exponent coincidence, and for metallic materials, the Wiedemann-Franz law [81] would imply that, for a given temperature, knowing the value of the electrical conductivity means that the thermal value can be predicted, and vice versa.

5. Influence of Porosity on Magnetic Properties

Powder metallurgy processing is used both in the manufacture of soft (e.g., electric transformer cores) and hard magnetic materials (permanent magnets). The interest of this technique lies in being a near-net shape process, with almost no further processing and good final magnetic properties. Soft magnetic parts in electromagnetic circuits are quickly magnetised and demagnetised by a magnetic field, to transform an electrical signal into motion or vice versa. The automotive industry is one of the main users of this magnetic functionality [82].

The knowledge of the correlations between magnetic properties and porosity could help to optimise properties and manufacturing processes. Unfortunately, studies on the influence of porosity on the magnetic properties of sintered materials are very scarce, especially for wide ranges of porosity variation. This is not because such influence does not exist; obviously, magnetic properties do vary with the porosity degree. Nevertheless, there are indeed works correlating magnetic and mechanical properties [83,84].

From a magnetic point of view, materials are characterised by the hysteresis curve, which is a representation of the magnetisation strength H versus the magnetic induction B. Concerning soft magnetic materials, the main properties to consider are (i) the saturation induction, B_{max}, (ii) the remanent induction, B_R, (iii) the maximum magnetic permeability,

μ_{max}, and (iv) the coercive field, H_c. The presence of porosity in sintered materials influences all these magnetic properties, although not in the same way [85–90].

Since the saturation and the remanent induction depend on the amount of material per unit volume, they will decrease with the presence of porosity. The dependence, at least in the porosity range between 0 and 0.25, can be considered approximately linear and expressed as:

$$B_{max} = B_{max0}(1 - a\Theta) \tag{11}$$

$$B_R = B_{R0}(1 - b\Theta) \tag{12}$$

where the parameters B_{max0}, a, B_{R0} and b can be determined experimentally. It has been found that for pure Fe, the values are B_{max0} = 1.55 T and a = 2.25, and B_{R0} = 1.31 T and b = 2.32 [80].

On the other hand, pores of sintered materials constitute anchoring points of the magnetic domain walls, so their presence causes a reduction in the maximum permeability and an increase in the coercive field. Thus, assuming a linear dependence, it can be said that:

$$\mu_{max} = \mu_{max0}(1 - c\Theta) \tag{13}$$

$$H_C = H_{C0}(1 + d\Theta) \tag{14}$$

with $\mu_{max0} = 6800 \cdot \mu_0$ (being $\mu_0 = 4\pi \times 10^{-7}$ T·m/A) and c = 2.79 [86] and H_{C0} = 55.71 A/m and d = 6.86 [87], for pure iron. For magnetic permeability, the linear relationship has been proven up to porosities of 0.1, and for magnetic coercivity up to porosities of 0.2.

The limitation to linear laws does not seem to be due to the conviction that they describe the real dependence on porosity, but rather to the lack of data to validate other non-linear models over wide porosity ranges. There is no reason to believe that the behaviour is linear, in view of the behaviour verified for other properties analysed in this work.

One possible reason for the lack of studies trying to elucidate the porosity dependence of magnetic properties over wide porosity ranges is that a low level of porosity is always desirable. (In fact, processes such as hot compaction are employed to manufacture magnetic materials in order to achieve a high density [85,91].) A more convincing reason is that magnetic properties not only depend on the porosity but are also strongly affected by pore morphology in the sense that domain wall anchoring increases with the irregularity of the pore shape. If this dependence were stronger than that due to the porosity itself, then correlations of magnetic property with porosity would be very difficult to validate. This is the conclusion that Jiles et al. arrived at in their study [92], in which they investigated the magnetic properties of six porous iron compacts with porosities in the range 0.3–6.2% and pore sizes in the range 1.6–13.2 µm. They left open the possibility that such correlations could be elucidated by careful work to ensure that only porosity varies, and that all other variables, such as pore size and grain size, remain constant. To complicate the problem, in addition to the presence and morphology of pores, another factor is particularly critical: the influence of chemical composition fluctuations is much greater than that of porosity. In fact, even very small percentages (in the order of a few ppm) of elements such as C, N, and O drastically reduce the permeability and strongly increase the value of the coercive field in iron compacts [93]. Precise control of this contamination can be difficult during the sintering process. Thus, the scatter of the experimental results is generally high, which might explain the difficulty in establishing a general mathematical relationship.

Nevertheless, results for sintered iron samples [94] show an evident non-linear relationship between porosity and coercivity. A non-linear relationship of both magnetic induction and coercivity with porosity has also been found for sintered iron samples [95]. Moreover, the influence of pore concentration and morphology on the maximum or saturation induction has been found according to a power law expression (Archie's law):

$$B_{max} = B_{max0}(1 - \Theta)^n \tag{15}$$

where the parameter n depends on the pore shape and ranges from 1.5 to 3 [96–98].

In the absence of other non-linear expressions, it seems reasonable to use the power law of Equation (1), which has been confirmed to describe the dependence on porosity of the rest of the properties analysed. Thus, the following expressions could be proposed:

$$B_{max} = B_{max0}(1 - \Theta/\Theta_{\mathrm{M}})^{n} \tag{16}$$

$$B_{R} = B_{R0}(1 - \Theta/\Theta_{\mathrm{M}})^{m} \tag{17}$$

$$\mu_{max} = \mu_{max0}(1 - \Theta/\Theta_{\mathrm{M}})^{p} \tag{18}$$

$$H_{C} = H_{C0}(1 - \Theta/\Theta_{\mathrm{M}})^{q} \tag{19}$$

where n, m and p are positive, and q negative, fitting constants. Note how the exponent in Equation (19) is a negative value, to ensure that the property grows with increasing porosity. Note also that Equation (15) is a particular case of the more general Equation (16).

The validity of the proposed equations is analysed in Figure 6. The fitting of the linear law, Archie's law and percolation law to the relative saturation induction, remanent induction, maximum permeability and relative coercivity is shown. Cores from iron powder were prepared by sintering in hydrogen for 30 min at 1120 °C, cooled at a rate of 5.5 °C per minute [99] for the three first properties. Coercivity was measured on iron powder compacted at 600 MPa and sintered at 1200 °C for 2 h and 1300 °C for 16 h [94]. The saturation induction of the fully dense material was 1.6 T, the remanent induction 1.5 T, the maximum permeability $6900{\cdot}\mu_0$, and the coercivity 60 A/m.

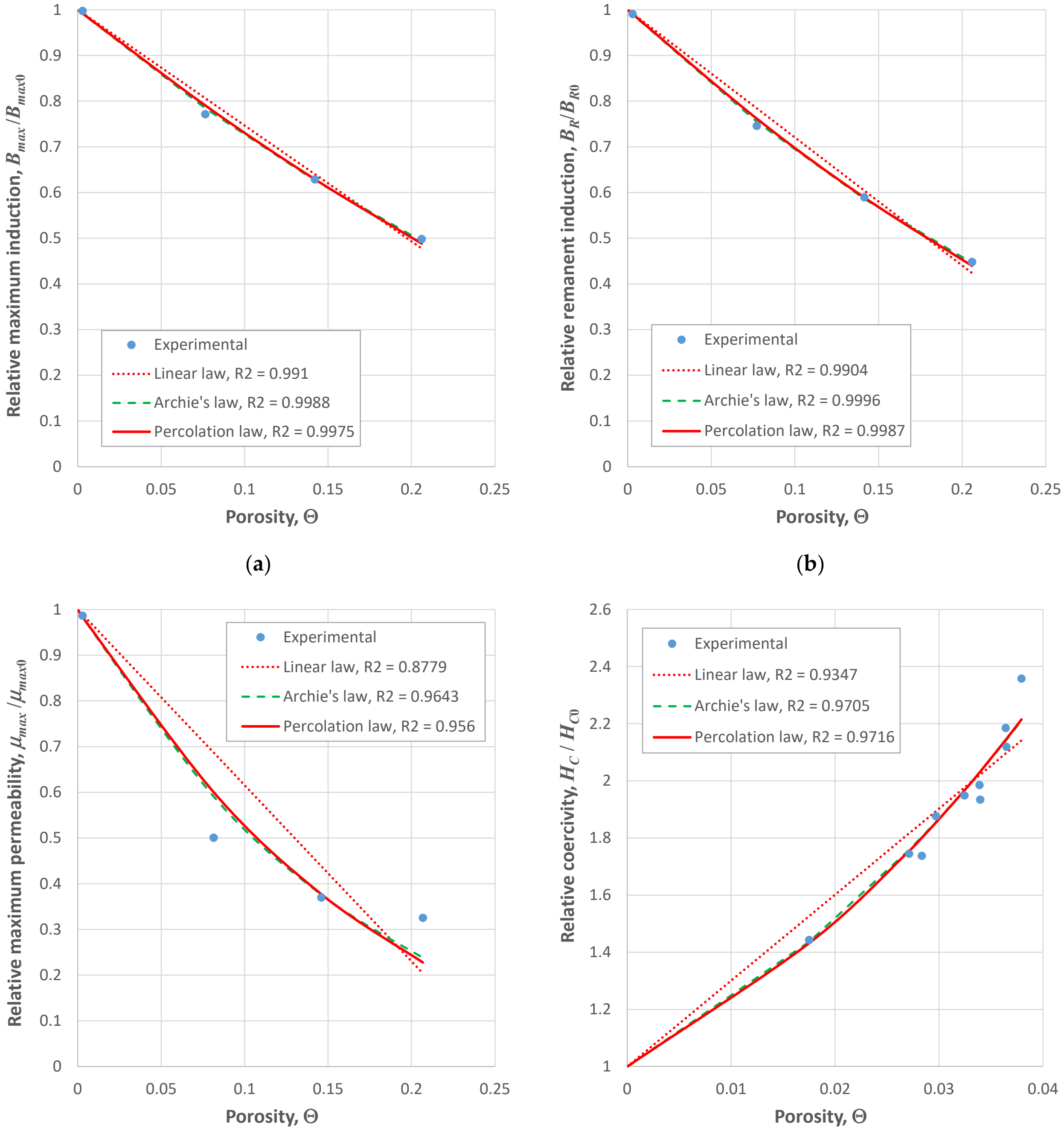
The scarce amount of experimental data for the saturation and remanent induction makes it difficult to say which law is best fitted. The obtained Θ_{M} value of 0.65 in both properties fitting with the percolation law is a proper value for iron powder. The exponents result n = 1.9 and m = 2.1 in the saturation and remanent induction fittings. Regarding permeability and coercivity, the power-type laws are clearly superior. The values of Θ_{M} are 0.6 and 0.5, respectively, the latter being far from the expected value for iron powders. The higher curvature observed in the graphs for these properties makes the exponents reach higher values than in any of the previous analysed properties, being p = 3.5 and q = −10, respectively. Nevertheless, the percolation law is shown as a good candidate to represent the behaviour of the studied materials.

The coercivity data found in some literature works show a confusing trend change. For example, in Lenel [99] and Jiles et al. [92], the variation of the coercivity with porosity shows a curvature contrary to that shown in Figure 6d, as revealed in Figure 7. This trend cannot be described by any of the previously analysed equations, not even by the percolation law. Nevertheless, as shown in Figure 7, it could be fitted by a variant of the percolation law:

$$H_{C} = H_{C0}(1 + \Theta/\Theta_{\mathrm{c}})^{q} \tag{20}$$

with q positive and lower than 1.

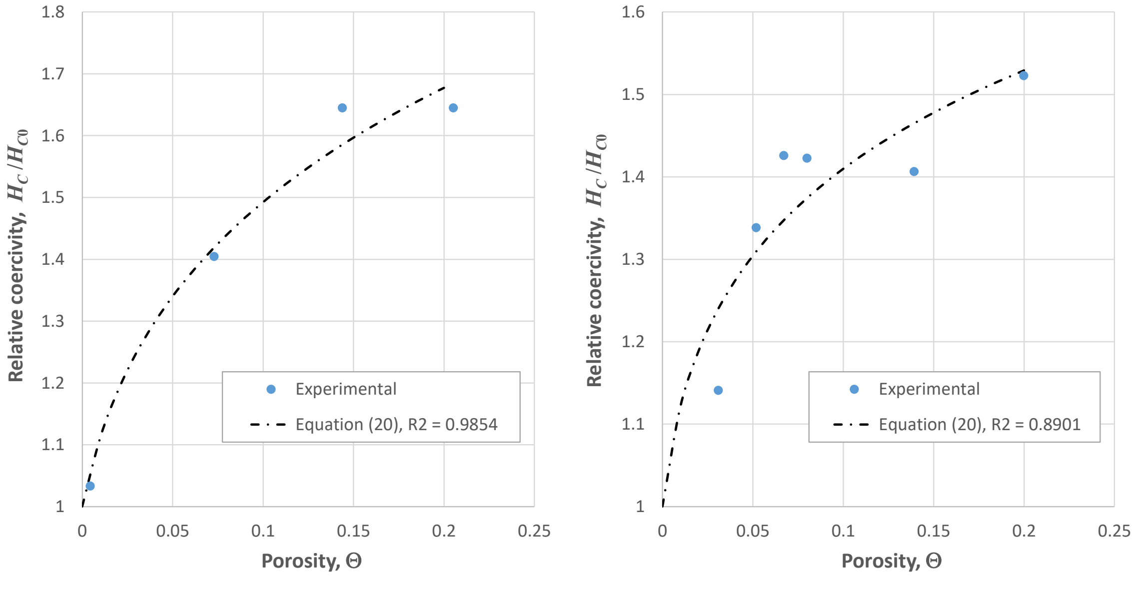
The best fitting in Figure 7a is obtained for values of Θ_{c} = 0.013 and q = 0.184, and for Figure 7b of Θ_{c} = 0.007 and q = 0.123. The low value of the parameter Θ_{c} in both cases leads to the conclusion that Θ_{c} cannot be identified with the maximum porosity of the powdered system. In order to know whether this is a real behaviour or the result of parameters not under control during the sintering process, a more detailed study is required. Unfortunately, it is not possible to find more recent works dealing with this issue.



(**a**) (**b**)

(**c**) (**d**)

Figure 6. Experimental values of: (**a**) relative saturation induction vs. porosity [99]; (**b**) relative remanent induction vs. porosity [99]; (**c**) relative maximum permeability vs. porosity [99]; (**d**) relative coercivity vs. porosity [94], and fitting with the linear law, Archie's law and the percolation law.



(**a**) (**b**)

Figure 7. Alternative behaviour of the coercivity vs. porosity according to: (**a**) Lenel [99] and (**b**) Jiles et al. [92], and fitting with the Equation (20).

6. Conclusions

The influence of porosity on the main elastic properties, ultimate strength, thermal and electrical conductivity, and magnetic properties has been analysed through different expressions proposed by researchers. The bibliographic study allows one to conclude that the elastic properties and the electrical/thermal conductivities have received more attention from the researcher community. Lower attention has been paid to magnetic properties, restricted to materials with a very low porosity content. This different degree of attention seems unjustified, considering that most of the expressions proposed to model a certain property could be tested to describe others, mainly because of sharing the same physical boundary conditions. The lower number of equations proposed for some properties may be due to the higher influence on them of microstructural aspects such as pore size and shape (secondary for other properties), which makes it difficult to establish well-defined correlations.

A joint analysis of all the proposed equations leads to the conclusion that most of them can be applicable in the low porosity range. Only some of the analysed equations satisfy the physical limits expected for sintered powdered materials, especially because the limit corresponding to the maximum porosity must be identified with the tap porosity (or a maximum porosity level) of the starting powder. All the expressions intended to cover the whole physical range of porosity are non-linear.

Among all the proposed expressions, the expression here called the percolation law has been proved to be a valid law for the whole range of porosities of sintered materials and all the analysed properties. According to the coefficients of determination (R^2) of the fittings to experimental data, it seems to be the most sensitive and reasonable option. The inclusion of two possible fitting parameters guarantees a better agreement with the experimental data for those properties with sensitivity not only to the porosity level, but also to the size and morphology of the pores.

The percolation equation has been proposed by different researchers and in different contexts, with variations regarding the exponents of this power law. In some cases, this is a fixed parameter (a constant or an experimentally measurable value), leaving the equation without free fitting parameters and therefore being valid to predict materials' behaviour. Other variations propose an exponent totally free that must be determined by fitting the equation to experimental data of the analysed property. Nevertheless, it is difficult to reach a precise conclusion regarding the value of the exponent without analysing the experimental data of the studied property. The analysed data in this paper indicate that the exponent takes values in the order of 1.72 for the Young's modulus, 2.5 for the ultimate strength, 2.6 for hardness, 1.44 for the electrical conductivity, 1.11 for the thermal conductivity, and 1.9–3.5 in magnetic properties except for the coercivity, which has a higher value of 10.

The development and proposal of simple mathematical expressions to model the dependence of the properties of sintered materials with their total porosity was a research challenge during the decades of the 1960s–1980s. A large number of expressions were proposed, mainly for mechanical and electrical/thermal transport properties. The verification of the large influence of the pores' morphology and connectivity restrained these works. From a retrospective view, comparative studies checking the application of the proposed expression for properties of a different nature are quite limited. It has also been found that, among the proposed models, only percolation models contain a parameter to describe the global nature of the powder; e.g. the tap porosity. In summary, it was still desirable to have a comparative analysis on all the theoretical studies then proposed. In addition to the academic interest, the main objective of these works is still maintained: the use of simple expressions, based on the property of the bulk material, the total porosity, and some other parameters (experimentally easy to measure or obtained from indirect test) to estimate the property of a porous sintered material.

Nevertheless, the actual trend based in massive computation is totally necessary. It allows for knowing the influence of every detail of the porosity. However, this new trend should coexist with simpler mathematical models, mainly valid for first approaches.

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