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On the asymmetrical dependence of the threshold pressure of infiltration on the wettability of the porous solid by the infiltrating liquid

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A general equation has been derived for the threshold pressure of infiltration of liquids into porous solids. From this equation all the known equations for the threshold pressure can be obtained, using different assumptions on the morphology of the porous solid and on the way how the liquid infiltrates the solid. Particularly, the Young-Laplace equation, the Carman-equation, and the modification of the Carman equation, suggested by White and later by Mortensen and Cornie have been reproduced as particular cases of the general equation. A new particular solution of this general equation is also suggested, taking into account that the original solid/gas interface inside the porous body is not fully replaced by the solid/liquid interface during infiltration, especially for the case of non-wetting liquids. The new, general equation consists of three semi-empirical parameters, which should be found experimentally for a given type of morphology of the porous solid and for the given ratio of the surface tension to the density of the infiltrating liquid metal. The new equation provides a value of the threshold contact angle to be between 65.5° and 90°, depending on the morphology of the porous solid. Consequently, the threshold pressure appears to be an asymmetrical function of the contact angle. Based on the new equation, the practical constancy of the threshold pressure is predicted in the interval of the contact angles between 120° and 180°.

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1. Introduction

For the infiltration of non-wetting liquids into porous solids an external pressure is required, which should be above threshold pressure, (P_{th}) for successful infiltration.

The threshold pressure is a complex function of the morphology of the porous solid, physical properties of the infiltrating liquid, and the contact angle between the liquid and the solid. The threshold pressure is in fact the negative of the so-called capillary pressure. The simplest model for the capillary (threshold) pressure, valid for cylindrical capillaries, is known since the works of Young and Laplace (see [1]).

Further, Carman [2] in 1941 modified the Young-Laplace equation for porous solid with random morphology and a perfectly wetting fluid. The modified equation included the average porosity, particles size and particle shape factor. This model was found very useful, but was limited in its application due to the zero contact angle. Therefore, the Carman model was extrapolated to the case of non-perfectly wetting liquids by White [3] in 1982 and by Mortensen and Cornie [4, 5] in 1987–1990. The result of such a derivation appears to be the Carman equation, multiplied by the cosine of the contact angle.

According to all the above models, the threshold pressure is a symmetrical function of the cosine of the contact angle, around the value of $\Theta = 90^\circ$. The value of 90° can be called the 'threshold contact angle', below which spontaneous infiltration occurs.

The extended Carman equation was applied for the last 15–20 years in many papers for the interpretation of the experimental results [6–15]. This equation was even used to estimate the contact angle in different liquid metal/solid ceramic systems [16–20], but the results were usually different from the "real" contact angle, determined from the sessile drop experiments. In literature there are some experiments [8, 21, 22] where the threshold contact angle was found below 90°. It means that the threshold pressure in reality is not a

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symmetrical function of the contact angle, and so the Carman equation, extended in [3–5] should be further modified.

There have been a number of theoretical papers of these and other authors [23–26], predicting that the threshold contact angle is below 90°. The goal of the present work is to extend the Carman equation for a random porous solid structure, taking into account that the original solid/gas interface is not fully replaced by the solid/liquid interface during infiltration, especially for non-wetting systems. It will turn out that the resulting threshold contact angle appears to be below 90° and the threshold pressure appears to be an asymmetrical function of the contact angle.

2. The general equation of the capillary pressure

Let us imagine a solid particle of any shape, situated at the liquid/gas interface, being immersed partly in the liquid. The interfacial force, acting on this particle in the direction, perpendicular to the liquid/gas interface, was recently derived as follows [27, 28]:

$$F = \sigma \cdot \left(\frac{dA_{\mathrm{sl}}}{dh} \cdot \cos\Theta - \frac{dA_{\mathrm{lg}}}{dh} \right) \tag{1}$$

where F is the force (N), σ is the surface tension of the liquid (N/m), A_{sl} is the solid/liquid interface area (m^2), A_{lg} is the liquid/gas interface area (m^2), Θ is the contact angle of the liquid on the solid (degree) and h is the path, along which the particle travels perpendicular to the liquid/gas interface, from outside towards inside of the bulk liquid. When a particle is situated on the top of a liquid phase, the interfacial force will be pulling the particle into the liquid if $F > 0$, or pushing it out, when $F < 0$. On the other hand, if the particle is fixed in the space, the interfacial force will be pulling the liquid on its surface when $F > 0$, or will be pushing it away from it, when $F < 0$. In this latter case, A_{sl} and A_{lg} are considered to be the total solid/liquid and liquid/gas interfacial areas inside the porous body.

When the interfacial force is divided by A_{plane}, the plane projection of the total area of the liquid/gas infiltration front (perpendicular to the infiltration direction), the capillary pressure (P_{c}) is obtained, acting in the direction of the infiltration:

$$P_{\mathrm{c}} = \frac{\sigma}{A_{\mathrm{plane}}} \cdot \left(\frac{dA_{\mathrm{sl}}}{dh} \cdot \cos\Theta - \frac{dA_{\mathrm{lg}}}{dh} \right) \tag{2}$$

The threshold pressure of infiltration by definition equals the capillary pressure, taken with a negative sign: $P_{\mathrm{th}} = -P_{\mathrm{c}}$.

3. The capillary pressure for the cylindrical capillary

Let us imagine a large amount of a liquid with a fixed, cylindrical capillary of inner radius R_{c}, partially immersed into it and situated perpendicularly to the liquid/gas interface with the liquid, covering an inner wall of the capillary with height h. Let us consider the liquid moving slowly up along the capillary, with no distortion of the shape of the infiltration front. Then, the interfacial areas can be calculated as: $A_{\mathrm{sl}} = 2R_{\mathrm{c}}\pi h$ and $A_{\mathrm{lg}} = kR_{\mathrm{c}}^2\pi$ (k depends on Θ), and the plane projection of the infiltration front will be: $A_{\mathrm{plane}} = R_{\mathrm{c}}^2\pi$. Substituting these expressions into Equation 2, the following equation is obtained for the capillary pressure:

$$P_{\mathrm{c}} = \frac{2}{R_{\mathrm{c}}} \cdot \sigma \cdot \cos\Theta \tag{3}$$

Equation 3 is the well-known Young-Laplace equation. As follows from Equation 3, $P_{\mathrm{c}} > 0$, i.e. the capillary pressure will be pulling the liquid into the capillary, if $\Theta < 90°$. Thus, the threshold contact angle of infiltration, according to the capillary model is 90°. From Equation 3 one can also see that the capillary (and the threshold) pressure is a symmetrical function of the cosine of the contact angle.

4. The capillary pressure for a perfectly wetting liquid, infiltrating into a porous solid of random microstructure

Let us consider a porous solid with a total cross sectional area A (parallel to the liquid/gas interface), with a random microstructure and with an average porosity ε. For simplicity, let us imagine that the infiltration front is macroscopically flat. Let us consider a moment of penetration, when the liquid is infiltrated into the solid at a height h. Then, the liquid/gas interface area will have a constant value, i.e. $A_{\mathrm{lg},0} = \varepsilon A = \text{const}$.

In order to express the solid/gas interface area, let us introduce S, as a specific surface area of the solid particles. The unit of S is m^2/m^3 = m^{-1}, i.e. the surface area of the average particle, available for an infiltrating liquid, divided by the volume of the average particle. For a spherical particle of radius R: $S = 3/R$, while for a long cylindrical fiber of radius R: $S = 2/\mathrm{R}$ (neglecting the end correction).

Now, let us consider a volume of Ah of the porous body before infiltration. The sub-volume Ah(1-ε) will equal the volume of the solid phase inside this porous solid. Then, the total surface area of all the particles can be obtained by multiplying this sub-volume by the specific surface area of the particles: $A_{\mathrm{sg}} = \mathrm{Ah}(1-\varepsilon)\mathrm{S}$. When the infiltrating liquid of perfect wettability (with zero contact angle) infiltrates this porous body, all the initial solid/gas interface will be replaced by the solid/liquid interface, therefore $A_{\mathrm{sl},0} = A_{\mathrm{sg}} = \mathrm{Ah}(1-\varepsilon)\mathrm{S}$. The average plane projection area can be obtained as: $A_{\mathrm{plane},0} = \mathrm{A}\varepsilon$.

Substituting these geometrical expressions into Equation 2, taking into account $\cos\Theta = 1$, the following equation can be obtained:

$$P_{\mathrm{c},0} = S \cdot \frac{1-\varepsilon}{\varepsilon} \cdot \sigma \tag{4}$$

Equation 4 is equivalent to the Carman's Equation [2]. It should be mentioned that Carman did not actually derive the capillary pressure, he rather derived the equilibrium height of infiltration [2]. However, our Equation 4 follows from his equation in a straightforward way.

5. A simple extension of the Carman's equation to non-perfectly wetting liquids

In the first approximation, for the case of non-perfectly wetting liquids ($\Theta > 0°$) the same geometrical equations can be taken valid: $A_{\mathrm{sl}} = \mathrm{Ah}(1\text{-}\varepsilon)\mathrm{S}$, $A_{\mathrm{lg}} = A\varepsilon = \text{constant}$, $A_{\mathrm{plane}} = A\varepsilon$. Substituting these expressions into Equation 2 for $\cos\Theta < 1$, the following equation can be obtained:

$$P_{\mathrm{c}} = S \cdot \frac{1-\varepsilon}{\varepsilon} \cdot \sigma \cdot \cos\Theta = P_{\mathrm{c},0} \cdot \cos\Theta \qquad (5)$$

Equation 5 is identical with the equation, derived by White [3] and by Mortensen and Cornie [4, 5]. Equation 5 predicts the threshold contact angle being equal to 90° and the capillary (and threshold) pressure is a symmetrical function of the contact angle. Thus, these conclusions [3–5] are identical with the conclusions from the classical Young-Laplace equation, the only difference being that the geometrical coefficient $2/R_{\mathrm{c}}$ in Equation 3 is replaced by $S(1\text{-}\varepsilon)/\varepsilon$ in Equation 5.

6. An improved extension of the Carman's equation to non-perfectly wetting liquids

According to the derivation of Equation 5, the total initial solid/gas interface within a porous body is assumed to be replaced by the solid/liquid interface during infiltration. In other words, the infiltration is presumed to proceed without porosity formation, even for non-wetting liquids, independent of the morphology of the porous solid body. However, a large number of experimental evidence exists for proving the opposite: non-perfectly wetting, and especially non-wetting liquids will not be able to infiltrate all the free space in porous solids. These liquids will leave some porosity in the porous body, even after the bulk infiltration is completed [29–31].

In the present paper, a general equation will be derived, taking into account this effect, by introducing some semi-empirical parameters.

6.1. Extension of the Carman's equation to perfectly non-wetting liquids

For a perfectly non-wetting liquid ($\Theta = 180°$), the final solid/liquid interface ($A_{\mathrm{sl},180}$) will be lower than the initial solid/gas interface (A_{sg}) in the porous body, as the liquid will not be able to penetrate all the pores. Let us define the semi-empirical coefficient k_1 ($0 < k_1 < 1$) as the ratio of $A_{\mathrm{sl},180}$ to A_{sg}. Then, the following equation can be written:

$$A_{\mathrm{sl},180} = k_1 \cdot A \cdot h \cdot (1-\varepsilon) \cdot S \qquad (6\mathrm{a})$$

If the liquid is not in full contact with the solid wall of the porous body, the liquid/gas interfacial area will be higher compared to the perfectly wetting case. The liquid/gas interface area can be divided into two parts: parallel and perpendicular to the infiltration direction h. Parallel to the infiltration direction, the liquid/gas interface area will be some k_2-part of the non-wetted solid/gas interface area (with $0 < k_2 < 1$). Parameter $k_2 < 1$ (when $k_1 < 1$), as the infiltrating liquid tends to minimize its free surface area, and thus it will take a shape of distorted, curved cylinders (with possible interlinks between them). Perpendicular to the infiltration direction, the liquid/gas interface area will remain constant as an average over the large area A. Then, the liquid/gas interface area can be written as:

$$A_{\mathrm{lg},180} = k_2 \cdot (1-k_1) \cdot A \cdot h \cdot (1-\varepsilon) \cdot S + \text{const} \quad (6\mathrm{b})$$

Let us also modify the plane projection of infiltration front (perpendicular to the infiltration direction) by the semi-empirical coefficient k_3 ($0 < k_3 < 1$). Then, the plane projection of the infiltration front can be written as:

$$A_{\mathrm{plane},180} = k_3 \cdot A \cdot \varepsilon \qquad (6\mathrm{c})$$

Now, let us substitute Equations (6a–6c) into Equation 2. After re-arrangements, the following equation is obtained:

$$\begin{aligned} P_{\mathrm{c},180} &= -S \cdot \frac{1-\varepsilon}{\varepsilon} \cdot \sigma \cdot \frac{k_1 + k_2 - k_1 \cdot k_2}{k_3} \\ &= -P_{\mathrm{c},0} \cdot \frac{k_1 + k_2 - k_1 \cdot k_2}{k_3} \end{aligned} \qquad (7)$$

As follows from Equation 7, generally $P_{\mathrm{c},180} \neq P_{\mathrm{c},0}$, and thus the capillary (and the threshold) pressure generally will be an asymmetrical function of the contact angle. The condition of symmetry at the two ends of the $P_{\mathrm{c}} - \cos\Theta$ diagram will be kept only, if $k_3 = k_3{*}$ (see curve B of Fig. 1), where $k_3{*} = k_1 + k_2 - k_1 k_2$, what is generally not the case.

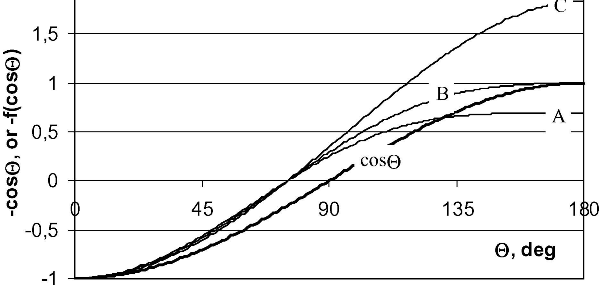

Figure 1 Dependence of the function -f(cosΘ) (being proportional to the threshold pressure) on contact angle, compared to the $-\cos(\Theta)$ function. Parameters: $k_1 = 0.1$, $k_2 = 0.5$ (for curves A, B and C), $k_3 = 0.8$ (curve A), $k_3 = k_3{*} = 0.55$ (curve B) and $k_3 = 0.3$ (curve C).

6.2. Extension of the Carman's equation to liquids of any wettability

Let us interpolate between functions $P_{c,0}$ and $P_{c,180}$, to obtain the general function $P_{c,\Theta}$, being approximately valid at any contact angle. For that, the interfacial areas A_{sl}, A_{lg} and A_{plane} should be first defined as function of the contact angle.

In the first approximation, from comparison of A_{sl} for the two boundary cases, the following equation can be written:

$$A_{sl,\Theta} = \frac{1}{2}\cdot[(1+k_1)+(1-k_1)\cdot\cos\Theta]\cdot A\cdot h\cdot(1-\varepsilon)\cdot S \tag{8a}$$

In Equation 8a the semi-empirical coefficient k_1 was interpolated from 1 (valid for $\Theta = 0°$) till its minimum value of k_1 (valid for $\Theta = 180°$) by a simplest linear function of the cosine of the contact angle. The value of the liquid/gas interface area can be written analogously, from Equation 6b:

$$A_{lg,\Theta} = k_2\cdot\left\{1-\frac{1}{2}\cdot[(1+k_1)+(1-k_1)\cdot\cos\Theta]\right\}\cdot A\cdot h\cdot(1-\varepsilon)\cdot S + \text{const} \tag{8b}$$

For the calculation of the plane projection of the infiltration front, the dependence of the semi-empirical parameter k_3 on the contact angle will be described by a similar function, as it was done for k_1. Then, one can obtain:

$$A_{plane,\Theta} = \frac{1}{2}\cdot[1+k_3+(1-k_3)\cdot\cos\Theta]\cdot A\cdot\varepsilon \tag{8c}$$

Substituting Equations (8a–c) into Equation 2 the following equation is obtained:

$$P_{c,\Theta} = S\cdot\frac{1-\varepsilon}{\varepsilon}\cdot\sigma\cdot f(\cos\Theta) = P_{c,0}\cdot f(\cos\Theta) \tag{9a}$$

where

$$f(\cos\Theta) = \frac{(1+k_1+k_2-k_1\cdot k_2)\cdot\cos\Theta+(1-k_1)\cdot(\cos^2\Theta-k_2)}{(1+k_3)+(1-k_3)\cdot\cos\Theta} \tag{9b}$$

From comparison of Equations 4, 7, 9a, and b one can see that the function $P_{c,\Theta}$ reduces to $P_{c,0}$ at $\Theta = 0°$ and to $P_{c,180}$ at $\Theta = 180°$.

6.3. The final equation for threshold pressure and its analysis

Finally, the threshold pressure can be written as the negative of Equation 9a:

$$P_{th} = -S\cdot\frac{1-\varepsilon}{\varepsilon}\cdot\sigma\cdot f(\cos\Theta) \tag{10}$$

As follows from Equation (10), the threshold pressure is proportional to $-f(\cos\Theta)$ with all other parameters kept constant. The function $-f(\cos\Theta)$ is plotted against the contact angle in Fig.1, for three particular sets of parameters. One can see that this function is indeed different from the classical $-\cos\Theta$ function, even when $k_3 = k_3*$ (see Fig. 1.case B.).

One can also see from Fig. 1 that the threshold contact angle (i.e. the contact angle at which the $-f(\cos\Theta)$ function crosses zero) is significantly lower than 90°. The equation for the threshold contact angle can be obtained by making Equation 9b equal 0. It follows that the threshold contact angle will be a complex function of only 2 parameters: k_1 and k_2 (see Fig. 2). The minimum possible value of the threshold contact angle is 65.5° (corresponding to $k_1 = 0$ and $k_2 = 1$). The maximum possible value of the threshold contact angle is 90°, corresponding to $k_1 = 1$. A realistic value of the threshold contact angle is around 75°, corresponding to $k_1 = 0.1$ and $k_2 = 0.5$. A similar value (between 70° and 80°) was obtained experimentally by Yang *et al.* [8, 21].

For large (close to 1) values of parameter k_3 and low (close to zero) values of parameter k_1 the threshold pressure becomes almost independent of the contact angle in a relatively wide contact angle interval below 180° (see Fig. 1.case A). Let us introduce a variable Θ_{const}, with a meaning that $f(\cos\Theta_{const}) = 0.9f(\cos 180°)$. It means, that if the threshold pressure is measured with an accuracy of ±5%, the threshold pressure seems to be independent of the contact angle in the interval between Θ_{const} and 180°. The dependence of the Θ_{const} value on parameter k_3 (at fixed values of k_1 and k_2) is shown in Fig. 3. One can see that Θ_{const} has its lowest value (120° for $k_1 = 0.1$ and $k_2 = 0.5$) at $k_3 = 1$. Thus, it is quite realistic to get an approximately constant value of the threshold pressure in the interval of the contact

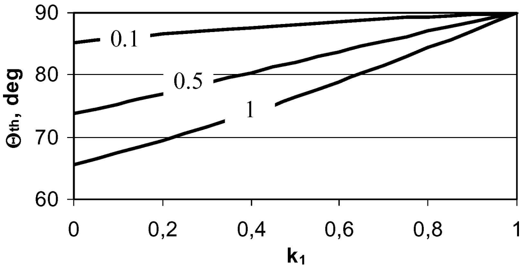

Figure 2 Dependence of the threshold contact angle on parameter k_1 as function of the value of parameter k_2 (numbers are given on the curves).

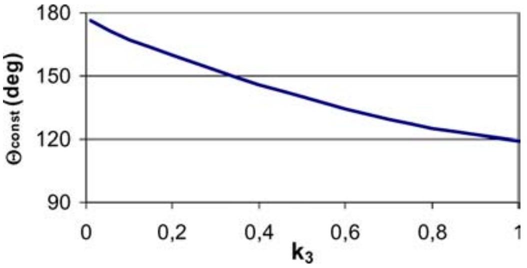

Figure 3 The dependence of parameter Θ_{const} on parameter k_3 at $k_1 = 0.1$ and at $k_2 = 0.5$.

angles between 120° and 180°. This theoretical prediction is confirmed by some experimental results [11, 13, 14, 18]. Garcia-Cordovilla *et al.* found that the threshold pressure can be described by a joint semi-empirical graph for different solid materials, infiltrated by the same liquid, indicating that the role of the contact angle was negligible for the non-wetting systems, studied by them [11, 14, 18]. Candan, Atkinson and Jones [13] even concluded that for different non-wetting systems studied by them experimentally, it is most reasonable to use $\Theta = 180^\circ$ if the results are interpreted by Equation 5, rather than using different contact angles, measured in independent experiments.

In order to find the values of parameters k_1, k_2 and k_3, further theoretical and experimental work is needed. In this paper let us only predict that all the three semi-empirical parameters k_1, k_2 and k_3 will be functions of the morphology of the porous solid and the physical properties of the liquid metal, probably through the dimensionless quantity $\sigma S^2/g\rho$. Before these relationships are established, the present Authors suggest the following average values to be used: $k_1 = 0.1$, $k_2 = 0.5$, $k_3 = 0.8$ (see Fig. 1, curve A).

7. Conclusions

A general expression for the capillary pressure of infiltration has been derived (Equation 2). The well-known equations of Young-Laplace (Equation 3), of Carman (Equation 4) and of White and of Mortensen-Cornie (Equation 5) are all particular cases of this equation, corresponding to different morphologies of the porous solid and to the way the infiltrating liquid behaves. In the present paper the new expression was obtained, taking into account that non-perfectly wetting liquids will not be able to infiltrate porous solids without remaining porosity (Equations 9a and b). As demonstrated in Fig. 1, this new relationship provides a new functional dependence of the threshold pressure of infiltration on the contact angle, compared to the classical relationships, being proportional to the cosine of the contact angle. As a consequence, the classical Carman equation and its modified version by White and by Mortensen and Cornie should be used to estimate the contact angle in the given liquid/solid system with a special care. Further experimental and theoretical work is needed to estimate the three semi-empirical parameters of this model as function of the morphology of the porous body and the properties of the liquid.

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