ON CAPILLARY EQUILIBRIUM IN A MODEL OF A POROUS BODY WITH INTERSECTING PORES OF VARIABLE CROSS SECTION

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Abstract

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ON CAPILLARY EQUILIBRIUM IN A MODEL OF A POROUS BODY WITH INTERSECTING PORES OF VARIABLE CROSS SECTION

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To determine the effective parameters of porous electrodes, it is important to know the characteristics of the boundary between the liquid and the gas filling the pores (^{1}). In (^{2}) the problem is solved in simplified form, since the pore radius is assumed constant. In the present work an attempt is made to take into account simultaneously the intersection of pores and the variation of their cross section along their length.

Consider a porous body bounded on one side and situated in the half-space $x > 0$. To the left of it, under a certain pressure excess relative to the liquid, there is a gas which penetrates into the body through pores whose radius is greater than the critical one. The magnitude of the critical pore radius is determined by the pressure drop and the properties of the liquid (^{1}). We shall seek the conditional probability that an arbitrary pore in a given cross section is filled with gas, if it is known that in this cross section the pore is supercritical (i.e., its radius is greater than the critical radius). In what follows only these conditional probabilities are considered; for brevity we shall simply call them probabilities.

The following is assumed concerning the structure of the porous body. The pores constitute a system of randomly arranged, intersecting cavities of circular cross section with continuously varying radius. The body is homogeneous, i.e., the probability of finding at some point a pore with prescribed characteristics does not depend on the coordinates. The true length of a pore l is assumed to be related to its projection onto the x-axis by the relation $l = \beta x$, where β is the tortuosity. At intersections of pores it is assumed that no more than three pores can meet at one point, i.e., each pore can branch into two. We are concerned with supercritical branching, in other words with such an intersection of pores in which all three meeting pores are supercritical. The point at which a pore branches will be called a node. The process of pore branching will be regarded, using the terminology of probability theory, as a Markov-type process, stationary and ordinary. These assumptions, apparently, are not far from the truth, since from consideration of the technology of preparation of porous bodies it is clear that the formation of branching is a random process which can occur at any point of a pore and does not depend on when and how the pore branched

Fig. 1

Figure 1: Fig. 1

earlier. Consequently, the probability of branching of a pore over a length dx, to within quantities $o(dx)$, is equal to $\nu\,dx$. If the radius of a pore at some point falls to the critical value, then such an event will be called the "death" of the pore. This process, like the process of branching, will be considered Poissonian. Thus, the probability of "death" of a pore over a length dx, provided that in the cross section x it is supercritical, is, to the same accuracy, equal to $\lambda\,dx$. The constants ν and λ for a given porous body depend only on the pressure drop. However, for the time being we leave the question of this dependence out of consideration. In solving the problem, we shall regard ν and λ as known.

Let us introduce the following classification of pores and nodes. Branching nodes will be divided into bifurcation nodes and merging nodes. By bifurcation nodes (nodes of type F) we shall mean such nodes to which one pore approaches from the left and two from the right. By merging nodes (nodes of type G) we shall mean nodes to which two pores approach from the left and one from the right.

To classify the pores, let us draw, through two infinitely close points x and $x+dx$, sections perpendicular to the x-axis (Fig. 1). The pores passing through the section x are divided into four types. A pore of type B will mean a pore that "dies" in the layer $(x, x+dx)$. A pore of type C bifurcates, and a pore D merges in the layer $(x, x+dx)$. E is a pore with which, in the layer $(x, x+dx)$, no events occur. The pores passing through the section $x+dx$ are divided into the types B', C', D', E'. The notation is analogous to the preceding one. Their meaning is clear from the drawing.

Membership of a pore in one or another type will be called an event. The events B, C, D, and E (as well as B', C', D', E') form a complete group of pairwise incompatible events. Let us find their probabilities.

From the preceding it follows that

$$P(B) + P(C) + P(D) + P(E) = 1;$$

$$P(B) = \lambda\,dx; \tag{1}$$

$$P(C) + P(D) = \nu\,dx; \tag{2}$$

$$P(E) = 1 - (\lambda + \nu)\,dx. \tag{3}$$

Fig. 1

By symmetry considerations $P(F) = P(G)$; since one pore (of type C) approaches each branching node from the left, while two pores (of type D) approach each merging node from the left, we have $P(D) = 2P(C)$, and consequently

$$P(C) = \frac{1}{3}\nu\,dx; \tag{4}$$

$$P(D) = \frac{2}{3}\nu\,dx. \tag{5}$$

In exactly the same way,

$$P(B') = \lambda\,dx; \tag{6}$$

$$P(C') = \frac{1}{3}\nu\,dx; \tag{7}$$

$$P(D') = \frac{2}{3}\nu\,dx; \tag{8}$$

$$P(E') = 1 - (\lambda + \nu)\,dx. \tag{9}$$

While filling the porous body, the gas moves in a complicated manner, repeatedly changing the direction of its motion. Therefore we shall compute the probability of filling a pore with gas in the following way. First let us find the probability of filling if the gas, penetrating into the porous body, moves from its surface (from zero) to infinity only from left to right, not filling those pores through which it would have had to move from right to left; such a process will be called cycle number 1. Then let us find the probability of filling if the gas, having completed cycle number 1, moves from infinity to zero, filling all the pores into which it can enter while moving only from right to left; such a process will be called cycle number 2. Cycles number 3, 4, 5···are defined analogously.*

Let A_k denote the event consisting in the filling of an arbitrary supercritical pore passing through the section x after k cycles. The event consisting in the filling of an arbitrary supercritical pore passing through $x + dx$ will be denoted by A'_k, and, finally, the filling of nodes by A''_k. The ultimate aim of the work is to compute the probability of the event A_∞.

For brevity of notation, let $Y_k(x) = P(A_k)$ and $y_k(x) = P(A_k\overline{A}_{k-1})$. A bar over a letter, as usual, denotes the opposite event. Po-

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Fig. 2

Figure 2: Fig. 2

* The cycles considered are only a method for calculating the probabilities of filling and in no way claim to describe the kinetics of gas penetration into the pores.

since

$$A_k = \sum_{i=1}^{k} A_i \overline{A}_{i-1}$$

and the terms in this sum are pairwise incompatible, then

$$Y_k = \sum_{i=1}^{k} y_i.$$

Let us derive the equation for the first cycle. By definition $y_1 = P(A_1 \overline{A}_0)$. The event $\overline{A}_0$ is certain; hence $A_1 \overline{A}_0 = A_1$ and $y_1 = P(A_1)$. To derive the equation it is necessary to relate $y_1(x+dx)$ to $y_1(x)$.

The different types of pores that arise after the first cycle are shown in Fig. 2. Straight lines denote pores filled with gas, wavy lines those remaining with liquid. The classification of pores is also presented there. We note that

$$A_1' = (B' + C' + D' + E')A_1.$$

The event $B'A_1$ is impossible; consequently,

$$A_1' = C'A_1 + D'A_1 + E'A_1,$$

$$y_1(x+dx) = P(A_1') = P(C'A_1') + P(D'A_1') + P(E'A_1'). \tag{10}$$

Let us compute separately each term of this equality.

Fig. 2

By the multiplication theorem (3), the probability of the event $C'A_1'$ can be represented as the product of the probability of the event C' by the conditional probability of the event A_1' under the condition C':

$$P(C'A_1') = P(A_1'/C')\,P(C'). \tag{11}$$

The expression $P(A_1'/C')$ is the probability that a pore of type C' is filled. Such a pore will be filled if and only if the confluence node G to which it belongs is filled in the first cycle. Since the probability of the latter event is $P(A_1''/G)$, it follows that

$$P(A_1'/C') = P(A_1''/G). \tag{12}$$

Since the filling of a confluence node can occur along two independent paths (pores of type D) and the conditional probability that each such pore is gaseous is $P(A_1/D)$, then, according to Bernoulli' s scheme,

$$P(A_1''/G) = [P(A_1/D)]^2 + 2[1 - P(A_1/D)]P(A_1/D). \tag{13}$$

In view of the independence of the events A_1 and D,

$$P(A_1/D) = P(A_1) = y_1(x). \tag{14}$$

Substituting (7), (12), (13), and (14) into (11), we obtain

$$P(C'A_1') = [2y_1(x) - y_1^2(x)] \cdot \frac{1}{3}\nu\, dx. \tag{15}$$

Next, by analogy with (11) and (12), we have

$$P(D'A_1') = P(A_1'/D')\, P(D'); \tag{16}$$

$$P(A_1'/D') = P(A_1''/F) = P(A_1/C) = P(A_1) = y_1(x). \tag{17}$$

Together with (8), this gives

$$P(D'A_1') = y_1(x) \cdot \frac{2}{3}\nu\, dx, \tag{18}$$

and, finally,

$$P(E'A_1') = P(EA_1) = P(E)P(A_1) = y_1(x)\,[1 - (\lambda + \nu)\, dx]. \tag{19}$$

Substitute (15), (18), and (19) into (10) and pass to the limit $dx \to 0$. As a result we obtain

$$\frac{dy_1}{dx} + \left(\lambda - \frac{1}{3}\nu\right) y_1 + \frac{1}{3}\nu y_1^2 = 0. \tag{20}$$

Fig. 3

Figure 3: Fig. 3

The boundary condition for this differential equation is obtained from the fact that every supercritical pore opening onto the surface of the body must already be filled in the first cycle, i.e.,

$$y_1(0) = 1. \tag{21}$$

The solution of equation (20) with boundary condition (21) is the function

$$y_1(x) = \frac{3\lambda - \nu}{3\lambda e^{\mu x} - \nu}, \tag{22}$$

where $\mu = \lambda - \frac{1}{3}\nu$.

In the case $\mu = 0$,

$$y_1(x) = \frac{1}{1 + \frac{1}{3}\nu x}. \tag{23}$$

Fig. 3

The behavior of $y_1(x)$ at infinity (Fig. 3) is determined by the sign of μ. For $\mu > 0$, $y_1 \to 0$ as $x \to \infty$, while for $\mu < 0$,

$$y_1 \xrightarrow[x\to\infty]{} 1 - \frac{3\lambda}{\nu}.$$

Thus, depending on the relation between the constants λ and ν, gas in the first cycle penetrates into the body to a finite or infinite depth. In the latter case, the filling of the body at great depth becomes uniform (y_1 tends to a constant). This can occur if pressures are attainable at which the process of pore branching is more than three times as probable as the process of "death," i.e., $\nu > 3\lambda$.

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Note: Figure translations are in progress. See original paper for figures.

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