

CAPILLARY EQUILIBRIUM IN A POROUS SOLID MODEL 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 a liquid and a gas filling the pores [1]. The solution given in the paper [2] relates to a simplified version of the problem, for, the pore radius was taken to be constant here. In the present study it was attempted to make allowance for the pore cross section, and for the variation in cross section along the length of the pore.

We shall consider a porous solid bounded on one side and occupying the semispace $x > 0$. On the left of the solid there is a gas which, being kept under a pressure exceeding that of the liquid, penetrates into the solid via pores with radii greater than the critical value. The magnitude of the critical radius is determined by the pressure drop and the properties of the liquid [1]. We shall search for the nominal probability that an arbitrary pore in a given cross section is filled up if the pore in this cross section is supercritical (i.e., its radius exceeds the critical value). Only these nominal probabilities will be considered further and we shall refer to them simply by the term "probabilities."

As to the structure of the porous solid the following assumptions are made. The pores form a system of intersecting voids arranged at random and having cross sections of variable radius. The solid is homogeneous, i.e., the probability of finding a pore of given characteristics at any site is independent of the coordinates. The actual pore length l is taken to be related to its projection on the x -axis by the relationship $l = \beta x$, where β represents the tortuosity factor. As regards the pore intersections, it is supposed that no more than three pores can meet in a single point, i.e., each pore can branch out into two pores. We are dealing with supercritical branching, i.e., with such branchings that the three joining pores are supercritical. A point from which pores branch out will be called a junction. Using the terminology of the probability theory, we shall take that pore branching is a stationary and ordinary Markov process. Evidently, this assumption is not far from the truth, for, a consideration on the preparation of porous solids clearly shows that branching is a random process which may occur in any point of the pore and is independent of the time when, and of the place where, the pore has branched off previously. Hence, the probability that branching will occur in the pore length dx equals νdx with an accuracy in the order of $o(dx)$. The case that the pore radius drops below the critical value at some point will be called pore "destruction." This process and that of branching will be supposed to be of Poisson's type. Consequently, provided that the cross section of the pore at point x is supercritical, the probability of a destruction occurring in the length dx equals λdx within the limits of the above approximation. The values of ν and λ in a given porous solid depend only on the pressure drop. However, we shall not yet discuss this relationship. In solving the problem, we shall take ν and λ to be known.

We shall introduce the following classification of pores and junctions. The junctions will be distinguished into bifurcation junctions and confluence junctions. Junctions in which one pore from the left meet two from the right will be called bifurcation junctions (type F junctions). Junctions in which two pores from the left meet one from the right will be called confluence junctions (type G junctions).

To characterize the pores, we shall draw cross sections perpendicular to the x -axis in the points x and $x + dx$ (Fig. 1). The pores passing through the cross section in point x can be distinguished as four types: a pore which is "destroyed" in the interval $(x, x + dx)$ will be called a B type pore; a C type pore bifurcates; a D type pore shows confluence in the interval $(x, x + dx)$, and an E type pore is a pore in which nothing happens in the above interval. Among the pores passing through the cross section in the point $x + dx$, the types B', C', D', E' can be distinguished. The notation is similar to that used above and the meaning is clear from the figure.

The circumstance that a pore belongs to a given type will be called an "event." The events B, C, D, E (just like B', C', D', E') form a complete group of pairs of incompatible events. Let us look for the probabilities.

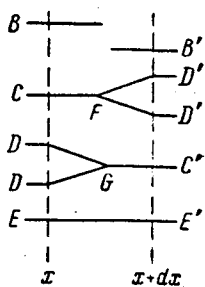


Fig. 1.

From the above considerations it follows that

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

$$P(B) = \lambda dx; \quad (2)$$

$$P(C) + P(D) = \nu dx; \quad (3)$$

$$P(E) = 1 - (\lambda + \nu) dx. \quad (4)$$

Symmetry considerations yield $P(F) = P(G)$; since in each bifurcation junction one pore (type C) comes from the left, and in each confluence junction two pores (type D) come from the left, $P(D) = 2P(C)$ and, hence

$$P(C) = \frac{1}{3} \nu dx; \quad (5)$$

$$P(D) = \frac{2}{3} \nu dx. \quad (6)$$

In exactly the same way

$$P(B') = \lambda dx; \quad (7)$$

$$P(C') = \frac{1}{3} \nu dx; \quad (8)$$

$$P(D') = \frac{2}{3} \nu dx; \quad (9)$$

$$P(E') = 1 - (\lambda + \nu) dx. \quad (10)$$

In filling up the porous solid, the gas moves in an erratic way, repeatedly changing its direction of flow. Therefore, we shall use the following procedure for computing the probability that a pore gets filled with gas. We shall first search for the probability that a pore gets filled up in the case that the gas penetrating into the porous solid moves from the surface ($x = 0$) to infinity from the left to the right, leaving unfilled those pores in which it has to move from the right to the left; we shall call this process cycle number 1. Then, we shall try to establish the probability of filling in the case where the gas, having completed cycle number 1, moves from infinity to zero, filling all pores in which it can penetrate only from the right to the left; this process will be called cycle number 2. The cycle numbers 3, 4, 5... are defined in a similar way.*

By A_k we designate the event that an arbitrary supercritical pore passing through the cross section x is filled after k cycles. The event that an arbitrary supercritical pore passing through the cross section $x + dx$ gets filled will be designated by A'_k , and the event that a junction gets filled, by A''_k . The ultimate aim of the paper is to compute the probability of the event A_∞ .

For brevity we introduce the notations $Y_k(x) = P(A_k)$ and $y_k(x) = (A_k \bar{A}_{k-1})$. In accordance with usual practice, a bar over a letter designates the opposite event. Since

$$A_k = \sum_{i=1}^k A_i \bar{A}_{i-1} \text{ and the terms in this sum denote pairs of incompatible events, it follows}$$

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

We shall derive the equation for the first cycle. According to the definition, $y_1 = P(A_1 A_0)$. Event A_0 is certain; hence, $A_1 A_0 = A_1$ and $y_1 = P(A_1)$. To permit derivation of the equation, $y_1(x + dx)$ must be related to $y_1(x)$.

The various pore types existing after the first cycle are shown in Fig. 2. Straight lines indicate pores filled with gas, wavy lines indicate pores still filled with liquid. The figure also illustrates the pore classification. We note that $A'_1 = (B' + C' + D' + E')A_1$. Event $B'A_1$ is impossible; consequently, $A'_1 = C'A_1 + D'A_1 + E'A_1$.

$$y_1(x + dx) = P(A'_1) = P(C'A_1) + P(D'A_1) + P(E'A_1). \quad (10)$$

We shall separately calculate each term of this equality.

* The cycles considered are no more than a method of computing the probabilities of filling, and do not at all pretend to describe the kinetics of gas penetration into the pores.

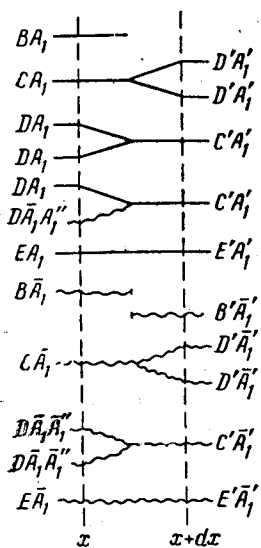


Fig. 2.

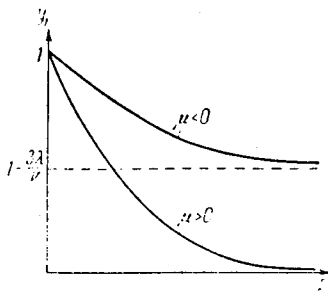


Fig. 3.

According to the multiplication theorem [3], the probability of event $C'A_1$ can be expressed as the product of the probability of even C' and the nominal probability of even A_1 under the condition C' :

$$P(C'A_1) = P(A_1/C') P(C'). \quad (11)$$

$P(A_1/C')$ is the probability that a C' type pore is filled. This type of pore is filled if, and only if, the confluence junction G to which it belongs is filled during the first cycle. Since $P(A_1^*/G)$ is the probability of the latter event, it follows that

$$P(A_1/C') = P(A_1^*/G). \quad (12)$$

Since a confluence junction can be filled in two independent ways (via the two D type pores) and each pore has the probability $P(A_1/D)$ of being filled with gas, it follows from Bernoulli's scheme that

$$P(A_1^*/G) = [P(A_1/D)]^2 + 2[1 - P(A_1/D)] P(A_1/D). \quad (13)$$

As the events A_1 and D are independent, we have

$$P(A_1/D) = P(A_1) = y_1(x). \quad (14)$$

Substitution of (7), (12), (13), and (14) in (11) gives

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

Further, in analogy to (11) and (12), we find

$$P(D'A_1) = P(A_1/D') P(D'); \quad (16)$$

$$P(A_1/D') = P(A_1^*/F) = P(A_1/C) = P(A_1) = y_1(x). \quad (17)$$

Instead of (8), this yields

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

and, finally,

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

Substituting (15), (18), and (19) in (10) and passing to the limit $dx \rightarrow 0$, we obtain

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

We find the boundary conditions of this differential equation from the circumstance that any supercritical pore starting from the solid surface is inevitably filled already in the first cycle, i.e.,

$$y_1(0) = 1. \quad (21)$$

The following function is the solution of Eq. (20) with the boundary condition (21)

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

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

In the case where $\mu = 0$

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

The behavior of $y_1(x)$ at infinitely large x is determined by the sign of μ (Fig. 3). At $\mu > 0$, $y_1 \rightarrow 0$, whereas at $\mu < 0$

$$y_1 \xrightarrow{x \rightarrow \infty} 1 - 3\lambda/\nu.$$

Depending on the relationship between the constants λ and ν , it follows therefore that in the first cycle the gas will penetrate into the solid to a finite or an infinite depth. In the latter case the degree of filling of the solid at a large depth becomes uniform (y_1 tends to a constant value). This may happen if pressures can be attained which are so high that branching is three times more probable than "destruction" (i.e., $\nu > 3\lambda$).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
