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Continuum description of quasi-static intrusion of non-wetting liquid into a porous body

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Abstract This paper proposes a continuum description of the quasi-static processes of non-wetting liquid intrusion into a porous body. The description of such processes is important in the interpretation of mercury porosimetry data, which is commonly used to determine the pore space structure parameters of porous materials. A new macroscopic model of capillary transport of non-wetting liquid in porous material is proposed. It is assumed that a quasi-static process of liquid intrusion takes place in the pore space-pressure continuum and that liquid filling an undeformable porous material forms a macroscopic continuum constituted by a mobile and a capillary liquid which exchange mass and energy. The capillary liquid forms a thin layer on the surface of the liquid filling the porous material that is in contact with the internal surface of the pores. It is immovable and contains the whole capillary energy. Mass balance equations for both constituents and constitutive relations describing capillary transport in the pore space-pressure continuum are formulated, and a boundary condition on the surface of the porous body is proposed. The equations obtained are solved for the special case of liquid intrusion into a ball of porous material. Analytical expressions are obtained for the saturation distribution of non-wetting liquid in the ball and for the capillary potential curve. Their dependence on parameters of the system is analyzed.

Keywords Non-wetting liquid intrusion · Continuum description · Diffusive model · Pore space-pressure continuum

1 Introduction

The modeling of quasi-static processes of non-wetting liquid intrusion into porous material plays an important role in the interpretation of experimental data (the so-called capillary potential curves) for mercury porosimetry obtained by mercury intrusion into a sample of porous material [22,23]. The parameters of the pore space structure, that is, the porosity and pore size distribution, the specific pore surface area and its distribution [14,17,18,23] and the tortuosity and permeability [2,9,21] are determined from these data. Simplified models of the microscopic pore space structure are used to interpret the experimental data. In mercury porosimetry, which is used by default to determine pore size distributions, the interpretation of experimental data is performed based on the capillary model of the pore space architecture. In this model, the pore space is formed by long capillaries of constant randomly distributed diameters that cross the whole sample. This provides a very simple description of the processes of mercury intrusion and allows direct interpretation of the experimental data.

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However, the course of these processes in a porous sample with capillary pore space architecture is considerably different from that found in real porous materials, in which the pore space is formed by a spatial network of channels with complex geometry and of random sizes. The distribution of mercury in porous samples with the capillary pore architecture is always homogeneous and is independent of their shape and size.

This problem does not occur in models with chain and network pore architecture. In the chain model, cylindrical tubes with a random distribution of diameters and lengths form a pore space composed of capillaries with stepwise changeable cross sections [4], whereas in the network models tubes, or cubic pores interconnected by cylindrical tubes, form a spatial network [1, 3, 6, 10, 20]. In this case, however, the mathematical description of mercury intrusion takes a very complex form and effective use of the network models requires numerical simulations.

There is no macroscopic description of the quasi-static processes of non-wetting liquid intrusion into porous material in the literature. The direct application of theories describes liquid transport in unsaturated porous materials to solve this problem, such as Richard's equations [16], produces results identical to those for the medium with capillary pore space architecture. This results from the assumption commonly taken in papers in this field that the capillary pressure is a constitutive quantity and is a unique function of saturation with liquid. Such constitutive assumption causes that character of distribution of both quantities in porous body is always the same. In this case, the homogeneity of the capillary pressure will always induce homogeneous distribution of saturation with liquid. For this reason, even the advanced thermodynamic models of two-phase flow in porous materials presented in papers [10–12] do not describe the inhomogeneity of liquid distribution during the quasi-static intrusion processes. Perhaps, the application of the second gradient theory of fluid displacement, proposed in the paper [15], makes such description possible. The second gradient theory is used in mechanics as a thermodynamical model of continuous media to study capillarity in fluids [5, 7, 8] and other phenomena [15, 19].

The aim of this paper is to formulate a new continuum description of the quasi-static process of non-wetting liquid intrusion into a porous body and to present an analytical solution of this problem for liquid intrusion into a ball of porous material.

The study is based on a new macroscopic physical model of capillary transport of liquid in porous materials formulated within the framework of multi-phase continuum mechanics. The model assumes that the quasi-static process of liquid intrusion takes place in the pore space-pressure continuum, that liquid filling an undeformable porous material forms a macroscopic continuum constituted by mobile liquid and capillary liquid and that the skeleton pore structure is isotropic. The capillary liquid forms a thin layer on the surface of the liquid filling the porous material that is in contact with the internal surface of the pores. It is immovable, contains the whole capillary energy and exchanges mass and energy with the mobile liquid in the vicinity of the menisci surfaces. The mobile liquid occupies an internal part of the liquid filling the pores and is surrounded by the film of capillary liquid and the menisci surfaces. It is assumed that the mobile liquid has the same properties as the liquid outside the pore space.

Balance equations were formulated for masses of both constituents and for the internal energy of the whole system and then used to derive part of the constitutive relations. Assuming the diffusive mechanism of menisci transport in the pore space-pressure continuum, a constitutive relation is proposed as fundamental for the description of non-wetting liquid intrusion into a porous body. Furthermore, a boundary condition is proposed that depends explicitly on the liquid pressure and pore diameter distribution on the surface of the body.

The boundary value problem is formulated in this paper for the description of liquid intrusion into a ball of porous material. The equation obtained takes the form of that for non-stationary diffusion, in which the pressure of the intruded liquid is present as an independent variable instead of time. The problem is solved analytically, and expressions for the saturation distribution of liquid in the ball, and for the capillary potential curve, are derived. Their dependence on parameters of the system is analyzed and the results are presented in the form of graphs.

2 Model assumptions

We consider the problem of quasi-static intrusion of a non-wetting liquid (e.g. mercury) into a porous body B of surface ∂B (Fig. 1) and of isotropic pore space structure. It is assumed that at the beginning of the intrusion process, the pores of the body are empty and the liquid surrounding the body has zero pressure. With the increase of pressure, liquid penetrates into the biggest pores of the body and its menisci are halted at the boundary of smaller pores. Due to the random character of the microscopic structure of the pore space, a non-homogeneous spatial distribution of liquid is formed inside the body which evolves as the pressure

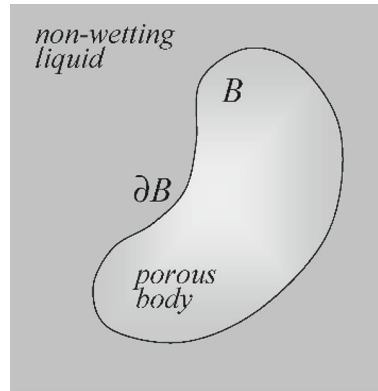


Fig. 1 Non-wetting liquid intrusion into a porous body

increases. The intrusion process is stopped when the pressure reaches a sufficiently high value to completely fill all of the pores.

To describe the process of quasi-static intrusion of non-wetting liquid into porous material, we formulate a new macroscopic model of capillary transport of liquid in porous materials within the framework of multi-phase continuum mechanics. In this model, the liquid filling the pore space of an undeformable porous material form a macroscopic continuum composed of two constituents: a mobile liquid and a liquid-like component called capillary liquid. The skeleton is assumed to be undeformable with an isotropic and homogeneous pore space, in which the transport processes take place. The division of liquid into two continua is justified from both a kinematic and energetic point of view. The capillary liquid is immovable and forms a film on the surface of the liquid filling the porous material that is in contact with the internal surface of the pores. This constituent includes all of the capillary energy and its physical properties differ significantly from the properties of the mobile liquid. The mobile liquid occupies the internal part of the liquid filling the pores and is surrounded by the film of the capillary liquid and the surfaces of the menisci. The mobile liquid is assumed to have the same physical properties as a liquid outside the pore space.

The capillary liquid exchanges mass and energy with the mobile liquid in the vicinity of the menisci surfaces and occurs only during the motion of the menisci in the pore space. In the quasi-static processes of non-wetting liquid intrusion into the porous body, liquid mass transport is closely related with the motion of the menisci. This allows modeling of the motion mechanisms of menisci in the pore space.

3 Balance equations

The macroscopic description of non-wetting liquid transport in an unsaturated porous material during the quasi-static process of intrusion is formulated within the framework of multi-phase continuum mechanics. Since the course of such a process is entirely determined by changes of the pressure in the intruded liquid, the transport of the non-wetting liquid in porous material will be considered as a process that takes place in the pore space-pressure continuum, just like the dynamic processes that take place in the space-time.

We assume that each constituent of the unsaturated porous material forms a material continuum, generally understood as a medium with continuous spatial distributions of mass and mass flux. This enables the basic notions of the kinematics of these constituents to be defined within the terms of spatial description of the medium.

3.1 Kinematics of the constituents

Taking into account the representative elementary volume dV of the unsaturated porous material in which all macroscopic quantities describing the kinematics of the mobile liquid and capillary liquid have appropriate stochastic representations, their masses dm , dm_c contained in this volume can be represented in the form:

$$dm = \bar{\rho}dV, \quad dm_c = \bar{\rho}_cdV \quad (3.1)$$

where $\bar{\rho}$, $\bar{\rho}_c$ are partial densities of the constituents. They are linked to the phase densities ρ , ρ_c by the relations

$$\bar{\rho} = f_v s \rho, \quad \bar{\rho}_c = f_v s_c \rho_c \quad (3.2)$$

where f_v is the volume porosity, and s , s_c (respectively) denote saturations of the medium with the mobile and capillary liquid. Saturation is defined as the ratio of the volume occupied by the given constituent in a representative sample of an unsaturated medium to the pore volume in that sample.

To define mass transport flux and velocity field of the mobile liquid induced by the pressure changes, we consider the representative elementary surface $d\mathbf{S}$ in the space region occupied by the porous body,

$$d\mathbf{S} = \mathbf{n} dS \quad (3.3)$$

where \mathbf{n} is a unit vector normal to this surface element and dS is its area.

The mass flux $d\Phi$ flowing through the surface element $d\mathbf{S}$ is linked to the vector of partial mass flux $\bar{\mathbf{q}}$ by the relation

$$d\Phi = \bar{\mathbf{q}} \cdot d\mathbf{S} \quad (3.4)$$

where the dot denotes the scalar product of vectors.

The partial mass flux $\bar{\mathbf{q}}$ represents the mass of the mobile liquid that flows through a unit area of surface perpendicular to the vector $\bar{\mathbf{q}}$ during the unit change of liquid pressure. It can be related to the phase flux \mathbf{q} of the mobile liquid by

$$\bar{\mathbf{q}} = f_v s \mathbf{q}. \quad (3.5)$$

We use the flux \mathbf{q} describing the mass transport of the mobile liquid to define the “velocity” field $\mathbf{v}(\mathbf{x}, p)$ of its motion in the space-pressure continuum. It takes the form

$$\mathbf{v}(\mathbf{x}, p) \equiv \frac{\mathbf{q}}{\rho}. \quad (3.6)$$

where by p the pressure in the mobile liquid is denoted. It is assumed that in the quasi-static processes this pressure is equal to the pressure in the liquid outside the porous body.

On account of the immobility of the capillary liquid, its mass flux $d\Phi_c$ flowing through the surface element $d\mathbf{S}$ is equal to zero,

$$d\Phi_c = 0. \quad (3.7)$$

3.2 Mass balance equations

Taking into account the immobility of the capillary liquid and the exchange of constituent mass with the mobile liquid, its local mass balance equation in the space-pressure continuum can be written in the form

$$\frac{\partial \bar{\rho}_c}{\partial p} = \bar{\psi} \quad (3.8)$$

where $\bar{\psi}$ represents a volume source of mass of the capillary liquid. This defines the mass of the capillary liquid exchanged with the mobile liquid in a unit volume of the medium for a unit change in the pressure p . It is related to the volume source ψ referred to a unit volume of the capillary liquid by

$$\bar{\psi} = f_v s_c \psi. \quad (3.9)$$

Considering the representations (3.1)–(3.6) for the mobile liquid, and in view of the exchange of mass between the mobile and the capillary liquid, the local mass balance equation for the mobile liquid in the space-pressure continuum can be written as follows

$$\frac{\partial \bar{\rho}}{\partial p} + \text{div}(\bar{\rho} \mathbf{v}) = -\bar{\psi}. \quad (3.10)$$

3.3 Internal energy balance equation for the whole system

Due to the very slow character of the quasi-static processes of non-wetting liquid intrusion into a porous body, we assume that there are no thermal effects in the system. With the mass densities of internal energy of the mobile and capillary liquid denoted by u and u_c , the internal energy balance equation for the whole system can be written in the form

$$\bar{\rho} \frac{Du}{Dp} + \bar{\rho}_c \frac{\partial u_c}{\partial p} - \text{tr}(\mathbf{DT}) + \boldsymbol{\pi}_{\text{mc}} \cdot \mathbf{v} - \bar{\psi}(u - u_c) = 0 \quad (3.11)$$

where \mathbf{T} is the Cauchy stress tensor in the mobile liquid and $\boldsymbol{\pi}_{\text{mc}}$ represents the volume interaction force exerted on the mobile liquid by the capillary liquid, which is caused by non-homogeneous distribution of the mobile liquid in the medium, whereas

$$\mathbf{D} = \frac{1}{2}(\nabla \otimes \mathbf{v} + \mathbf{v} \otimes \nabla), \quad \frac{D(\cdot)}{Dp} = \frac{\partial(\cdot)}{\partial p} + \mathbf{v} \cdot \nabla(\cdot).$$

4 Constitutive relations

The two mass balance equations (3.8) and (3.10) and the internal energy balance equation (3.11) contain nineteen unknown scalar fields:

$$\rho, \rho_c, s, s_c, u, u_c, \psi, \mathbf{v}, \mathbf{T}, \boldsymbol{\pi}_{\text{mc}},$$

which must be determined in order to ensure complete description of the quasi-static processes of non-wetting liquid intrusion into a porous body. This means that sixteen constitutive relations have to be formulated to close this system of equations.

We derive some of the constitutive equations assuming that the internal energies of the mobile and capillary liquid are unique functions of their mass densities,

$$u = u(\rho), \quad u_c = u_c(\rho_c), \quad (4.1)$$

and requiring the internal energy balance equation (3.11) to be satisfied identically for any quasi-static process in this system. Applying the constitutive relations (4.1), mass balance equations (3.8) and (3.10) and thermodynamic definitions of pressures in the mobile and capillary liquid,

$$p = \rho^2 \frac{du}{d\rho}, \quad p_c = \rho_c^2 \frac{du_c}{d\rho_c}. \quad (4.2)$$

the balance equation (3.11) can be written in the form

$$s f_v \frac{\partial \rho_c}{\partial p} \left(\frac{p}{\rho} + u - u_c - \frac{p_c}{\rho_c} \right) + f_v \left(p \frac{\partial s}{\partial p} + \rho_c \left(\frac{p}{\rho} + u - u_c \right) \frac{\partial s_c}{\partial p} \right) + \text{tr}(\mathbf{D}(\mathbf{T} + f_v s p \mathbf{I})) - \mathbf{v} \cdot (\boldsymbol{\pi}_{\text{mc}} - p \mathbf{grad}(s f_v)) = 0. \quad (4.3)$$

Taking into account that quantities

$$\frac{\partial \rho_c}{\partial p}, \quad \mathbf{D}, \quad \mathbf{v}$$

are independent, Eq. (4.3) will be satisfied identically for any quasi-static process in the system if the expressions in brackets at these quantities are equal to zero. We obtain the relations

$$u + \frac{p}{\rho} = u_c + \frac{p_c}{\rho_c}. \quad (4.4)$$

$$\mathbf{T} = -f_v s p \mathbf{I}, \quad (4.5)$$

$$\boldsymbol{\pi}_{\text{mc}} = p \mathbf{grad}_T(s f_v), \quad (4.6)$$

Equation (4.3) then reduces to the form

$$p \frac{\partial s}{\partial p} + p_c \frac{\partial s_c}{\partial p} = 0. \quad (4.7)$$

Relation (4.4) establishes local equality of mass densities of the total energies in the mobile and capillary liquids. Due to relations (4.1) and (4.2), equality (4.4) also establishes a unique relation between mass densities of both constituents. From (4.4), we have

$$\frac{d(\rho u)}{d\rho} = \frac{d(\rho_c u_c)}{d\rho_c},$$

Equality (4.7), in turn, can be interpreted as a balance equation of energy exchanged between the capillary and mobile liquids during the mass exchange between them. It shows that the sum of the work done by both liquids during the mass exchange is equal to zero. Considering that during the intrusion and extrusion processes changes of saturations in both liquids have the same direction, from equality (4.7), results that the pressure in the capillary liquid are always negative,

$$p_c < 0. \quad (4.8)$$

The negative pressure in the capillary liquid and its immobility resulting from direct contact with the skeleton, mean that this constituent should be treated as a solid-like.

The constitutive relations (4.1), (4.4)–(4.7) and the mass balance equations (3.8), (3.10) cause that the internal energy balance equation (3.11) is satisfied identically. This means that there we still lack of four constitutive relations. They should describe menisci motion in the pore space.

The vector quantity $\mathbf{v}(\mathbf{x}, p)$ characterizes the “velocity” of the motion of menisci in the medium during the quasi-static changes of the pressure p in the mobile liquid. Due to the non-dynamic mechanism of menisci motion in the pore space, this quantity should be defined by an independent constitutive equation. We assume a diffusive mechanism of menisci motion in the pore space-pressure continuum that is analogous to the diffusive motion of molecules that takes place in the space-time continuum. The menisci move with change of pressure in the mobile liquid jumping from one equilibrium position to another in a manner similar to the diffusion process observed in consecutive moments of time. It is therefore assumed that the mass flux of the mobile liquid moving together with the menisci is proportional to the gradient of saturation of the mobile liquid. In general, we have

$$\mathbf{v}(\mathbf{x}, p) = -C(s, p) \mathbf{grad}(s). \quad (4.9)$$

This is justified by the fact that this gradient may be considered as a local measure of the menisci surface, which defines the mass of mobile liquid transported together with the menisci. The minus sign appears in Eq. (4.9) because, as the pressure p increases, the direction of menisci motion is opposite to the direction of the saturation gradient of the mobile liquid. The constitutive relation (4.9) corresponds to Fick’s first law formulated in the theory of diffusion. However, there is a significant difference between the diffusion process and the process of quasi-static motion of liquid in unsaturated porous material: one takes place in the space-time continuum, where only the course of the processes defined by the direction of time changes is possible, while the other takes place in the space-pressure continuum, in which both directions of pressure changes are physically acceptable.

The coefficient $C(s, p)$ occurring in the constitutive equation (4.9) may, in general, be a function of both the saturation s with the mobile liquid as well as its pressure p . The functional form of this coefficient depends on the microscopic structure of the pore space and the wetting properties of the liquid and needs to be determined in experimental investigations.

Additionally, we assume that saturation with the capillary liquid during the intrusion process is a unique function of saturation with the mobile liquid,

$$s_c = s_c(s). \quad (4.10)$$

Constitutive relations (4.9) and (4.10) complete the system of equations describing quasi-static processes of non-wetting liquid intrusion into a porous body.

5 Boundary and initial conditions

In the process of non-wetting liquid intrusion into a porous body, the liquid penetrates only into pores with diameters greater than the critical diameter D^* which is related to the pressure p in the mobile liquid by Washburn's formula,

$$D^* = -4\sigma \cos(\theta)/p = \kappa/p, \quad (5.1)$$

where σ is the surface tension of the liquid and θ denotes the wetting angle of the skeleton surface.

Due to the random nature of the pore diameter distribution, the saturation $s_0^t(p)$ with the mobile and the capillary liquid on the body surface ∂B (Fig. 1) is directly defined by this distribution and the pressure in the intruded liquid. This requires formulation of the boundary condition for the problem of liquid intrusion depending on the pressure,

$$s^t(\mathbf{X}_b, p) = s_0^t(p), \quad (5.2)$$

To determine the explicit form of the function $s_0^t(p)$, we assume that the probability distribution of the pore diameter D on the body surface is given by the function $\varphi(D)$. Then, the function

$$\vartheta(D) = D^2/\overline{D^2}\varphi(D) \quad (5.3)$$

defines the surface measure of the probability density of pore diameter distribution on the body surface. In expression (5.3), the quantity $\overline{D^2}$ denotes the mean value of the square of the pore diameter.

Taking into account that at a given pressure in the liquid, all the supercritical pores (of diameter greater than D^*) on the body surface ∂B are filled, the saturation with liquid on this surface can be expressed by the formula

$$s_0^t(p) = \int_{D^*}^{D_0} \vartheta(D) dD \quad (5.4)$$

where D_0 is the maximum diameter of pores on the body surface.

As an initial condition for the problem under consideration, we assume the absence of liquid inside the body. For the pressure $p_0 = \kappa/D_0$, we have

$$s^t(R, p_0) = 0. \quad (5.5)$$

6 Liquid intrusion into a ball of porous material

We apply the macroscopic description of the quasi-static process of non-wetting liquid intrusion into porous body obtained in Sects. 3–5 to solve the boundary value problem of liquid intrusion into a ball of porous material. This can be used as a model of the process of mercury intrusion into a sample of porous material that takes place in the mercury porosimeters. This enables an analytical expression for the so-called capillary potential curve of porous sample directly obtained from mercury intrusion data, [22,23], to be derived. Description of such curves is necessary for interpretation of mercury porosimetry data.

6.1 Formulation of the problem

We shall consider the problem of quasi-static intrusion of a non-wetting liquid (e.g. mercury) into a ball of porous material of radius R_0 (Fig. 2) whose the pore space structure is homogeneous and isotropic.

It is assumed that all constituents in the system are incompressible. In this case, the process of liquid intrusion is described by mass balance equations (3.8) and (3.10) and constitutive relations (4.9) and (4.10). Due to the spherical symmetry of the problem under consideration, this system of equations can be reduced to one equation for saturation with the mobile liquid

$$\left(1 + \frac{\rho_c ds_c}{\rho ds}\right) \frac{\partial s}{\partial p} - \frac{1}{R^2} \frac{\partial}{\partial R} \left(C_s R^2 \frac{\partial s}{\partial R}\right) = 0 \quad (6.1)$$

where R is the radius coordinate of the spherical coordinate system.

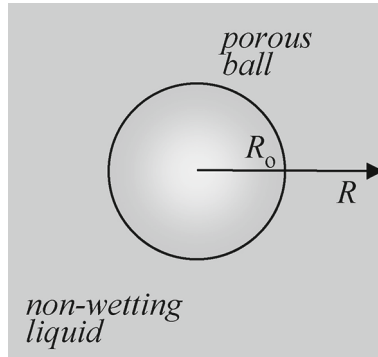


Fig. 2 Diagram of the system analysed

Assuming that the quantities ds_c/ds and Cs are constant, the saturation with the mobile liquid defines the saturation of the medium with both liquids

$$s^t(R, p) = s(R, p) + s_c(R, p) = (1 + ds_c/ds) s(R, p). \quad (6.2)$$

Then, Eq. (6.1) takes the form of linear non-stationary diffusion equation

$$\frac{\partial s^t}{\partial p} - C_o \frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial s^t}{\partial R} \right) = 0, \quad (6.3)$$

in which the mobile liquid pressure is present instead of time as the independent variable. For this reason, we will call constant quantity in (6.3),

$$C_o = Cs \left(1 + \frac{\rho_c ds_c}{\rho ds} \right)^{-1}, \quad (6.4)$$

the coefficient of the diffusive transport of menisci in the pore space during quasi-static process of liquid intrusion.

The boundary condition (5.2) and initial condition (5.5) for the problem of liquid intrusion into porous body, written for the ball, take the form

$$s^t(R_o, p) = s_o^t(p), \quad s^t(R, p_o) = 0 \quad (6.5)$$

where $s_o^t(p)$ is given by (5.4).

6.2 Solution of the problem

Applying new function $u(R, p)$ defined by the identity

$$u(R, p) \equiv Rs^t(R, p), \quad (6.6)$$

the boundary value problem described by Eq. (6.3) and the boundary and initial conditions (6.5) are simplified. We then obtain

$$\frac{\partial u}{\partial p} - C_o \frac{\partial^2 u}{\partial R^2} = 0. \quad (6.7)$$

$$u(R_o, p) = R_o s_o^t(p), \quad u(R, p_o) = 0. \quad (6.8)$$

Due to the inhomogeneity of the boundary condition (6.8)₁, we predict a solution of Eq. (6.7) in the form

$$u(R, p) = R s_o^t(p) + \sum_{n=1}^{\infty} A_n(p) \sin(a_n R) \quad (6.9)$$

where $a_n = n\pi/R_o$. Then, condition (6.8)₁ is satisfied for any values of coefficients $A_n(p)$.

Substituting expression (6.9) into Eq. (6.7) and using the Fourier sine expansion of the linear function R within the range $R \in \langle 0, R_0 \rangle$,

$$R = 2 \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{a_n} \sin(a_n R), \quad (6.10)$$

we obtain an inhomogeneous equation for the coefficients $A_n(p)$ of the form,

$$\frac{dA_n}{dp} + b_n A_n = 2 \frac{(-1)^n}{a_n} \frac{ds^0}{dp} \quad (6.11)$$

where $b_n = C_0 a_n^2$.

The general solution of Eq. (6.11) satisfying the initial condition (6.8)₂ is given by the expression

$$A_n = 2 \frac{(-1)^n}{a_n} \int_{p_0}^p \frac{ds^0}{du} e^{b_n u} du e^{-b_n p}. \quad (6.12)$$

Therefore, the distribution of the saturation with liquid $s^t(R, p)$ in the ball can be represented in the form of the convolution. From (6.6), (6.9) and (6.12), we obtain

$$s^t(R, p) = \int_{p_0}^p \psi(u) g_R(R, p-u) du \quad (6.13)$$

where

$$g_R(R, p) = 1 - 2 \sum_{n=1}^{\infty} (-1)^{n+1} e^{-b_n p} \frac{\sin(a_n R)}{a_n R}, \quad (6.14)$$

and the function $\psi(p)$, due to relations (5.4) and (5.1), is given by the formula

$$\psi(p) = \frac{ds^0}{dp} = \frac{\kappa}{p^2} \vartheta \left(\frac{\kappa}{p} \right). \quad (6.15)$$

The saturation distributions of non-wetting liquid in a porous ball during the quasi-static process of its intrusion are shown in Fig. 3. The graphs illustrate the course of the process of liquid intrusion described by

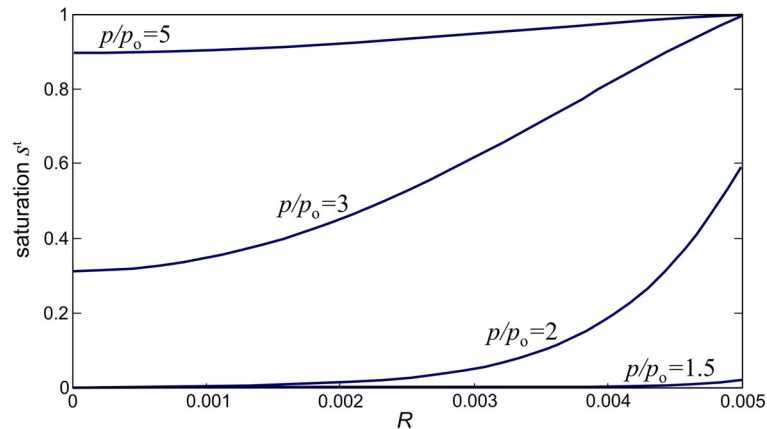


Fig. 3 Plots of the saturation distribution of non-wetting liquid in a porous ball of radius $R_0 = 0.005$ m during the quasi-static process of its intrusion. The graphs are plotted for different values of liquid pressure: $p/p_0 = 1.5, 2, 3, 5$, and the following values of system parameters: $D_0 = 10^{-3}$ m, $\alpha = \beta = 6$, $C_0 = 2 \cdot 10^{-9}$ m³s²/kg, $\tilde{C}_0 = C_0 p_0 / R_0^2 = 0.0998$

the formula (6.13), for the case of random distribution of pore diameters $\varphi(D)$ on the ball surface, given by a generalized beta distribution,

$$\varphi(D) = \frac{\alpha + \beta}{\pi D_0} \sin\left(\pi \frac{\alpha}{\alpha + \beta}\right) \frac{(D/D_0)^{\alpha-1} (1 - D/D_0)^{\beta-1}}{(D/D_0)^{\alpha+\beta} (1 - D/D_0)^{\alpha-\beta}}. \quad (6.16)$$

This distribution is defined on a finite range of pore diameters, $D \in \langle 0, D_0 \rangle$. Its parameters α and β satisfy the conditions: $\alpha + \beta > \alpha > 0$, and for $\alpha, \beta \geq 1$ it takes finite values. The graphs are plotted for the following values of system parameters: $R_0 = 5 \cdot 10^{-3}$ m, $D_0 = 10^{-3}$ m, $\alpha = \beta = 6$, $C_0 = 2 \cdot 10^{-9}$ m³s²/kg, $\bar{C}_0 = C_0 p_0 / R_0^2 = 0.0998$, and for different values of liquid pressure: $p/p_0 = 1.5, 2, 3, 4, 6$, where $p_0 = \kappa/D_0$, and for mercury $p_0 = 1247$ Pa. In this case, the boundary saturation changes with an increase in liquid pressure due to its penetration into pores of smaller and smaller diameter.

6.3 Description of the capillary potential curve

Capillary potential curves of samples of porous materials are obtained experimentally by the mercury intrusion method used for determining the pore size distributions. In this method, a sample of porous material is placed in a chamber called a penetrometer, the air is removed and the mercury is forced under pressure into the penetrometer. Two quantities are measured during this process: the volume of mercury intruded into the sample and its pressure. The normed graph relating both measured quantities is called the capillary potential curve. The pore size distribution and other parameters of the pore structure are determined based on this curve and on the various models of the pore space architecture and the process of mercury intrusion.

The expression (6.13) for the saturation distribution $s^l(R, p)$ with liquid in the porous ball enables derivation of a formula describing the capillary potential curve for a spherical sample of porous material.

Since the volume $V(p)$ of liquid intruded into the ball is given by the formula,

$$V(p) = \int_0^{R_0} 4\pi R^2 f_v s(R, p) dR, \quad (6.17)$$

on account of expressions (6.13) and (6.14), we obtain

$$\frac{V(p)}{V_0} = \int_{p_0}^p \psi(u) g(p-u) du \quad (6.18)$$

where $V_0 = 4/3\pi R_0^3 f_v$ is the volume of pores in the ball, while

$$g(p) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-b_n p}. \quad (6.19)$$

Expression (6.18) shows that in the proposed macroscopic model of the process of non-wetting liquid intrusion, the form of the capillary potential curves is determined by two random factors. The first is the pore diameter distribution $\varphi(D)$ on the surface of the porous ball which via Washburn's formula (5.2) determines the access of the non-wetting liquid to the sample pore space at various pressures. The second factor is the assumed model of the diffusive transport of menisci inside the sample, which is in general characterized by the coefficient $C(s, p)$ in the constitutive relation (4.9). Both factors are closely related to the pore size distribution in the porous sample. This implies the importance of the modeling of menisci diffusive transport for description of the capillary transport of liquid in unsaturated porous material.

Due to the assumed two-component model of liquid in pores characterized by different densities, the volume of liquid intruded into pores of the sample is not equal to the volume of liquid being intruded (outside the pores), whose measurement is the basis for formation of the capillary potential curves. However, because of the assumed incompressibility of the mobile and the capillary liquid, the relative volumes of liquid intruded into the pores and liquid being intruded are equal during the intrusion process. Therefore, expression (6.18) also describes the relative volume of liquid being intruded into the sample of porous material and represents a macroscopic model of the capillary potential curve of the ball.

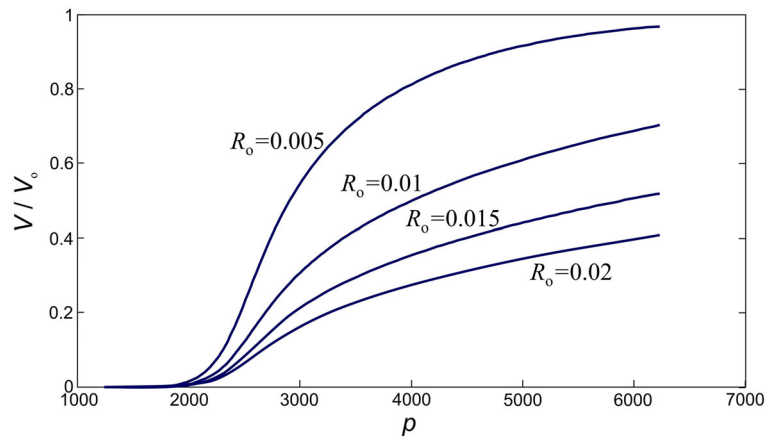


Fig. 4 Influence of the ball radius on the capillary potential curve for random pore diameter distribution on the ball surface ($D_o = 0.001$ m, $\alpha = \beta = 6$)

Figure 4 shows the graphs of the capillary potential curve described by expression (6.18). They express the dependence of the relative volume of non-wetting liquid intruded into the porous ball on the liquid pressure. Calculations were performed for four different values of the ball radius $R_o = 0.005, 0.01, 0.015, 0.02$ m, and for a constant coefficient of diffusive transport of menisci $C_o = 2 \cdot 10^{-9} \text{ m}^3\text{s}^2/\text{kg}$. The graphs show that the sample size of porous material is an important parameter determining the form of the capillary potential curves and should be taken into account when interpreting the mercury porosimetry data. Its impact may be limited, however, especially in the range of large pressures, by the dependence of the coefficient C_o of menisci transport on the liquid pressure and saturation, which was not taken into account in the description of liquid intrusion presented.

This requires detailed analysis and modeling of the diffusive transport of non-wetting liquid menisci in the pore space-pressure continuum. The experimental results presented in [13] indicate much smaller effect of sample size on the capillary potential curves than that illustrated in Fig. 4.

7 Final remarks

In the paper, a macroscopic description of the quasi-static process of non-wetting liquid intrusion into a ball of porous material has been presented. The description was based on a new physical model of capillary transport of liquid in unsaturated porous material that takes place in the pore space-pressure continuum. In this model, liquid filling the pore space form a macroscopic continuum composed of two constituents: mobile and capillary liquid exchanging mass and energy. The transport process of liquid menisci during pressure changes was assumed to be of the diffusive type. Mass balance equations, constitutive relations and boundary condition were formulated. It was shown that pressure in the capillary liquid is negative and that it should therefore be treated as solid-like constituent.

The equations obtained have been solved for the special case of liquid intrusion into a ball of porous material, and analytical expressions for saturation distribution with liquid and for the capillary potential curve were derived.

The proposed macroscopic model of the quasi-static process of non-wetting liquid intrusion into a sample of porous material enabled inclusion of all the major factors that determine the course of this process. These concern the shape and size of the sample, the boundary conditions on its surface and the mechanism of capillary transport of liquid within the sample. A detailed description of the influence of these factors on the process of liquid intrusion requires further investigation. The modeling of the mechanism of diffusive transport of liquid menisci in porous material characterized by the constitutive equation (4.9) and its connection with the pore size distribution in the porous body is of great importance for the proper description of these process.

The obtained results show that the mechanism of capillary transport of liquid in unsaturated porous materials should be included in a description of liquid and gas flow in such media. In the limit case, this process can be

considered as a disturbance of the quasi-static process or, conversely, the quasi-static process can be considered as a limit case of the stationary process.

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