

## Investigation of the structural properties of porous material according to the sorption isotherms and drainage curves

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In this paper in the compliance with the method of the local averaging, the basic relations of surface physics and thermodynamics for the description of diffusion process of the liquid and gas phases in the inhomogeneous porous media have been considered. In line with the drainage and sorption properties of the liquid in the porous skeleton, the normalized function of distribution of the pore size for the effective radius has been defined. The relations for the determination of the intrinsic and relative permeability of phases in the solid skeleton have been proposed. The dependence of the intrinsic permeability on the structural properties of porous material has been analyzed. A simple condition of the equilibrium of phases in the porous skeleton with surrounding medium has been obtained.

**Keywords:** *porous materials, adsorption, capillary phenomena, diffusion of gas and liquid*

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### 1. Introduction

The majority of porous structures may refer to the class of the mesoscopical divided materials. Investigation of such materials [1] can be performed by the experimental methods of microscopy and stereology according to the physical phenomena scattering and diffraction of electromagnetic waves or molecular adsorption from the liquid or gas phases. The reproduction of structure can be accomplished by the mathematical methods of statistical modeling or fractal analyses.

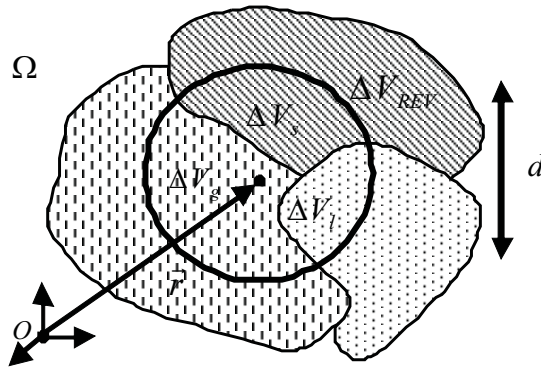
For the approximate description of continuous processes in the wet porous materials the most reasonable is usage of the averaging into the space the (local) [3] or the effective (macroscopic) [4] the middle values of physical quantity which can be obtained according to the function of distribution for sizes of pores from the effective radius [5] or methods of theory homogenization [6] by appropriate selection of the model for porous skeleton structure. For example, with assistance of the pore size distribution function in the approach of the laminar motion of liquid into the pore network which are simulated by the sets of interconnected capillaries with different radius it is possible to obtain the analytical expressions [7] for relative permeability [8] of the liquid and gas phases.

In this paper there has been demonstrated how the pore size distribution function for the effective radius can be obtained from the experimental sorption isotherms [9] or the drainage curves [10,11] of liquids retention. For this purpose the main relations of equilibrium [1,7,9,12] between phases in the porous wet material has been reviewed in conformity with the method of averaging in local space.

Due to the numerous experimental investigations [1] and model relations [9–11] for description drainage or sorption properties of liquid in the solid skeleton, there arises the necessity of systematization and selection of the optimal description of the structural properties for porous material.

The main purpose of presented publication is investigation of model parameters in the relations with intrinsic and relative permeability of phases into the porous structure according to the specified pore size distribution from the mean radius.

## 2. The volume characteristics of phases in the porous material. Principles of the local spatial averaging



**Fig. 1.** The depiction for the mesoscopic volume of averaging.

In the inhomogeneous multiphase porous media we can select the typical or characteristic mesoscopic volume of averaging  $\Delta V_{REV}$  (Fig. 1) (REV – Representative Elementary Volume)  $\Delta V_{REV} = \sum_{\alpha} \Delta V_{\alpha}$ , where  $\alpha = \{s, l, g\}$  is the index which corresponds to the solid ( $s$ ), liquid ( $l$ ) and gas ( $g$ ) phases,  $\Delta V_{\alpha}$  is the volume of  $\alpha$ -phase.

First of all, we must define the volume fractions of phases in the volume of averaging as  $\theta_{\alpha} = \Delta V_{\alpha} / \Delta V_{REV}$  ( $\sum_{\alpha} \theta_{\alpha} = 1$ ), then for the porosity of material we have

$$\varphi = (\Delta V_l + \Delta V_g) / \Delta V_{REV} = 1 - \Delta V_s / \Delta V_{REV} \quad (\varphi = \theta_l + \theta_g = 1 - \theta_s). \quad (1)$$

If define the local pore saturation with liquid  $\eta_l$  and gas  $\eta_g$  as

$$\eta_l = \Delta V_l / (\Delta V_l + \Delta V_g), \quad \eta_g = \Delta V_g / (\Delta V_l + \Delta V_g) \quad (\eta_l + \eta_g = 1), \quad (2)$$

then from the expressions (1) and (2) it follows that

$$\theta_s = 1 - \varphi, \quad \theta_l = \varphi \eta_l, \quad \theta_g = \varphi (1 - \eta_l). \quad (3)$$

According to the principle of local spatial averaging [3], the mesoscopic averaging volume (REV) (Fig. 1) has a constant spherical shape ( $d$  is the diameter of sphere) and is positioned arbitrarily ( $\mathbf{r}$  is the Cartesian coordinate of the center of the sphere) in a finite region  $\Omega$  of investigated microscopically porous material.

If on the boundaries of phase separation the physical laws of interaction [9] are known and the structure of the skeleton according to conditions of mesoscopically [1] may be represented then the way of deriving a spatially averaged (local) values of physical quantity [4] is quite simple because the method for calculation [2] of interaction between phases is described. For the obtaining of effective (macroscopic) values according to the theory of homogenization [6], there should be applied additional conditions for the periodic rapidly oscillating in the space functions of the studied physical quantity within the volume of irregularities of the structure (usually in a pore) under which the diffusion coefficients in the differential equations in the partial derivatives can be considered to be the constants as in the case of homogeneous material.

In some cases, as shown in [4], the effective value of physical quantity can be obtained as a local characteristic of porous material. Then such value is determined through the macroscopic (the averaged by distribution function [5]) parameters of the structure of porous material, volume fraction of phases and factors of external influence.

If the condition of static equilibrium is satisfied (the surface interfacial interaction is immovable) the volume fraction of phases is known at each point of the porous medium. Thus, we have to assert that the obtained by the method of spatial averaging, the local or effective values of the physical quantity are also continuous in the internal volume of investigated porous material.

### 3. The simple conditions of phase equilibrium in porous material. Definition of averaged capillary pressure

According to the Young-Laplace [9] equation and the Whitaker [2] theory of drying, a simple relation of equilibrium for averaged pressures can be written as follows

$$p_c = p_g - p_l = 2\sigma/r, \quad (4)$$

where  $p_c$  is the capillary pressure, which is defined by the effective radius of meniscus between liquid and gas phases  $r = \frac{1}{n} \sum_n r_n$  ( $1/r_n = 1/R_n^1 + 1/R_n^2$ ), here  $R_n^1$  and  $R_n^2$  are the main curvature radiuses,  $n$  is the number of surfaces separations between phases along the reciprocally connected capillaries,  $p_l$  and  $p_g$  are the pressures in the liquid and gas phases and  $\sigma$  is the surface tension coefficient.

By using the principles of local thermal equilibrium [2] ( $T_\alpha = T$ , here  $\alpha = \{s, l, g\}$ ,  $T_\alpha$  is the temperature of  $\alpha$ -phase, and  $T$  is the equilibrium temperature), we will describe a thermodynamic state of liquid and water vapor in the mesoscopic volume of averaging by means of Gibbs-Duhem [12] equations

$$-s_\nu dT + \frac{1}{\rho_\nu} dp_g + \frac{RT}{M_\nu x_\nu} dx_\nu - d\mu_\nu = 0, \quad -s_l dT + \frac{1}{\rho_l} dp_l - d\mu_l = 0, \quad (5)$$

where  $\beta = \{l, \nu\}$  is a symbolic notation of the liquid ( $l$ ) phase and the unsaturated water vapor ( $\nu$ ) component,  $G_\beta$  i  $S_\beta$  are the Gibbs energy and the entropy in the volume of averaging (REV),  $s_\beta = S_\beta/\Delta m_\beta$  is the specific entropy,  $\mu_\beta = G_\beta/\Delta m_\beta$  is the definition of the chemical potential,  $\Delta m_\beta$ ,  $\Delta V_\beta$  and  $\rho_\beta = \Delta m_\beta/\Delta V_\beta$  are the mass, the volume and the specific density, respectively,  $x_\nu = p_\nu/p_g$  is the molar fraction of water vapor,  $p_\nu$  and  $p_g$  are the partial pressures of the water vapor and the gas phase respectively,  $M_\nu$  is the molar mass of water vapor,  $R$  is the universal gas constant.

Due to the increments of chemical potentials in a state of the thermodynamic equilibrium of quasi-static process are equal ( $d\mu_\nu = d\mu_l$ ), based on the relations (4) and (5), considering the equation of state  $\rho_\nu = M_\nu p_g/RT$  (REV) under isothermal conditions, we can obtain the relation

$$(1 - \rho_l RT x_\nu/M_\nu p_\nu) dp_\nu - dx_\nu/x_\nu = 2\sigma x_\nu d(1/r). \quad (6)$$

For real gases, in particular the mixture of dry air and water vapor, the molar fraction of water vapor,  $x_\nu$  is the known function of partial pressure  $p_\nu$  and the temperature  $T$  according to the equation of state  $x_\nu = f(p_\nu, T)$  [13]. In the approximation of close to saturation ( $x_\nu \cong 1$ ) water vapor, it is possible assume that the quantity  $x_\nu$  is a constant ( $p_\nu \leq p_{\nu s}$ , were  $p_{\nu s} = p_{\nu s}(T)$  is the pressure of saturated water vapor). Then by integrating equation (6) with boundary conditions, which takes into account the fact that the pressure of a saturated water vapor  $p_{\nu s}$  corresponds to the average, the flat ( $r \rightarrow \infty$ ) surface of separation between phases ( $\lim_{r \rightarrow \infty} p_c = 0$ ), we obtain the Kelvin-Thomson [9] equation

$$p_c = 2\sigma/r = -\rho_l RT L n(\varphi)/M_\nu + \delta, \quad (7)$$

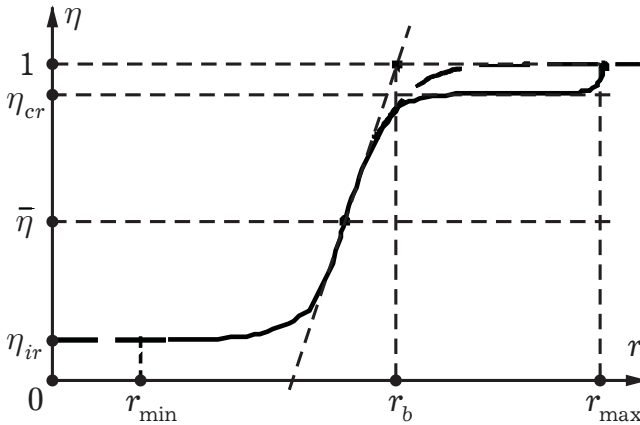
where  $\varphi = p_\nu/p_{\nu s}$  is the relative humidity of water vapor,  $\delta = p_\nu - p_{\nu s}$  is negligibly small with regard to the first item parameter.

### 4. The function of distribution of the pore sizes according to the effective radius

The finite region  $\Omega$  of the investigated porous sample with the total volume  $\Delta V_{spl}$  we can divide in the  $n$  elementary connected together and periodically repeated mesoscopic  $\Delta V_{REV}$  volumes of some constant geometric form.

Then the mean porosity  $\bar{\varphi} = 1 - \Delta V_s^*/\Delta V_{REV}$  of the material can be determined, where  $\Delta V_s^* = \frac{1}{n} \sum_i \Delta V_s^i$ ,  $i = \{1 \div n\}$  is the averaged volume of skeleton,  $\Delta V_s^i$  is the part of the solid phase

volume which indexed according to sequential disposition of the elementary volume  $\Delta V_{REV}$  in the finite region  $\Omega$  of the investigated porous sample.



**Fig. 2.** The distribution function of the pore saturation  $\eta$  with liquid depending on the effective radius  $r$  of meniscus.

$$\eta(\bar{r}_k) = \bar{\varphi}^{-1} \Delta V_l^*(\bar{r}_k) / \Delta V_{REV}, \quad k = \{1 \div n\} \quad (8)$$

where  $\Delta V_l^*(\bar{r}_k) = \frac{1}{n_k} \sum_{\bar{r}_i \in \Omega_k} \Delta V_l(\bar{r}_i)$  and  $\Omega_k = \{n_k \Delta V_{REV} : \bar{r}_i \leq \bar{r}_k\}$  is a set of the  $n_k$  volumes  $\Delta V_{REV}$  ( $\Omega_k \subseteq \Omega$ ) for which the effective radius is satisfied the inequality  $\bar{r}_i \leq \bar{r}_k$ ,  $\Delta V_l(\bar{r}_i)$  is the part of the liquid phase volume in the elementary volume  $\Delta V_{REV}$  for which the mean effective radius  $\bar{r}_i \in (r_{i-1}, r_i]$ .

It should be noted that  $\lim_{\bar{r}_k \rightarrow r_{\min}} \Delta V_l^*(\bar{r}_k) = \Delta \bar{V}_{ir}$  ( $\Delta \bar{V}_{ir} \cong 0$ ), where  $\Delta \bar{V}_{ir}$  is the residual volume of liquid phase, which corresponds to the water absorbed up to the surface of the solid skeleton. Such water, according to the drainage method, is impossible to remove from the porous material. Because  $\lim_{\bar{r}_k \rightarrow r_{\max}} \Delta V_l^*(\bar{r}_k) = \Delta \bar{V}_{cr}$ , ( $\Delta \bar{V}_{cr} \cong \Delta V_{REV}$ ), where  $\Delta \bar{V}_{cr}$  is the critical volume of liquid phase, so in accordance with the relation (8) ( $\eta_\alpha = \bar{\varphi}^{-1} \Delta \bar{V}_\alpha / \Delta V_{REV}$ , where  $\alpha = \{ir', cr'\}$  is symbolic denotations) we have the inequality:  $\eta_{ir} \leq \eta(\bar{r}_k) \leq \eta_{cr}$ ,  $k = \{1 \div m\}$ , here  $\eta_{ir}$  and  $\eta_{cr}$  is residual ( $\eta_{ir} \cong 0$ ) and critical ( $\eta_{cr} \cong 1$ ) saturations of pores with liquid, respectively.

We can obtain a typical example of the continuous dependence  $\eta = f(r)$  (Fig. 2) for the macroscopic volume  $\Delta V_{spl}$  of porous material on the basis of the experimentally found curves of sorption isotherms [9]:  $W = f(\varphi)$ , where  $W = \varphi \eta \rho_l / \rho_s$  is a moisture content ( $\rho_s$  and  $\rho_l$  are the densities of solid and liquid phases respectively) or drainage curves of liquid retention [7]:  $h = f(\eta)$ , where  $h = p_c / \rho_l g$  is the hydraulic head of liquid in the porous medium ( $g$  is a gravity acceleration), by using the relations (4) and (7) on moving up to the variables  $\eta$  and  $r$ .

From this dependence on the limits  $r \rightarrow r_{\min}$  and  $r \rightarrow r_{\max}$ , we have  $\partial \eta(r) / \partial r \rightarrow 0$ , so on the basis of the work [7] we can introduce a normalized function of pore size distribution for the mean radius

$$\Phi(r) = \frac{1}{\eta_{cr} - \eta_{ir}} r \frac{\partial \eta(r)}{\partial r} \quad \left( \int_{r_{\min}}^{r_{\max}} \Phi(r) dr = 1 \right), \quad (9)$$

as well as the effective pore saturation  $\theta$  with liquid

$$\Theta = \frac{\eta - \eta_{ir}}{\eta_{cr} - \eta_{ir}} = \int_{r_{\min}}^r \Phi(r) dr \quad (0 \leq \Theta \leq 1). \quad (10)$$

An interception point of the tangent to the dependence curve  $\eta = f(r)$  (Fig. 2) under the pore half-saturation with liquid ( $\bar{\eta} = 1/2$ ) and the axis of coordinate within the top boundary ( $\eta \rightarrow 1$ ) makes it possible to obtain an approximate value of the so called bubble pressure  $p_b \cong 2\sigma/r_b$ , where  $r_b$  is the mean radius of the detached gas bubbles at continuous filling of the pores with the liquid phase. The given pressure substantiates the definition of the critical saturation  $\eta_{cr}$  and gives grounds to state that according to (7) we have  $\lim_{\eta \rightarrow \eta_{cr}} p_c \cong p_b = \delta$ .

## 5. The flow equations in the saturated porous material. The Darcy law and Karman-Cozeny equation. The intrinsic permeability of the porous skeleton

When investigating the flow of liquid under gravity downward in a vertical tube filled up with the spherical particles of sand, Darcy [7] found the following:  $Q_l = -K_l A \Delta h / L$ , where  $Q_l$  is the volume flow of the liquid,  $\Delta h$  is the hydraulic pressure difference of the liquid in the manometers ( $L$  is the distance between them),  $A$  is the cross-sectional area of the tube,  $K_l$  is a proportional constant, which corresponds to the hydraulic conductivity of the liquid in the sand.

For one-dimensional plane case of full saturation of the pores with liquid ( $p_g = 0$  and  $\eta = 1$ ), the Darcy law can be generalized. To do this we define the relative to skeleton velocity of the liquid phase (superficial velocity) [7] as  $u_l = v_l - v_s$  (here  $v_l$  and  $v_s$  are the average velocities of the liquid and solid phases) in the line with the relation  $U_l = Q/A = \bar{\varphi} u_l$ , where  $U_l$  is the absolute velocity of the liquid (specific discharge), and  $\bar{\varphi}$  is the average porosity of the material. Since  $h = p_c / \rho_l g$  is the hydraulic head, then in the case of immovable state ( $v_s = 0$ ), the solid phase (stationary skeleton) for infinitely small increments of the length  $L$  we obtain

$$U_l = \bar{\varphi} v_l = -(K_l / \rho_l g) \partial p_c / \partial x = -k_s / \mu_l \partial p_c / \partial x, \quad (11)$$

here  $k_s = K_l \mu_l / \rho_l g$  is the intrinsic permeability of the porous skeleton,  $\mu_l$  is the dynamic viscosity of the liquid phase.

The intrinsic permeability is an absolute characteristic of the porous skeleton as pointed out by the well known Carman–Kozeny [5] equation

$$\rho_l g \Delta h / L = -\alpha_0 \psi^2 \tau \mu_l U_l (1 - \bar{\varphi})^2 / \bar{\varphi}^3, \quad (12)$$

where  $\psi = A_s / V_s$  is a specific surface of the solid phase ( $A_s$  and  $V_s$  are the total surface area and the volume of the solid phase, respectively),  $\tau = L_e / L$  is the tortuosity factor, in other words, the curving of capillaries in the pores ( $L_e$  is the mean length of the trajectory that is actually passed by a microparticle of liquid or gas in the porous medium between two parallel planes, which are perpendicular to the straight line of the length  $L$ ). The tortuosity factor is a constant, which depends on the configuration and properties of the porous skeleton.

Modeling the skeleton of porous medium with the aid of the spherical particles of the equivalent diameter  $d$  [5], we have  $\psi = 6/d$ . By comparing the relation (12) with the Darcy [7] law ( $K_l = \rho_l g k_s / \mu_l$ ) we obtain

$$k_s = (1/36\alpha_0) [\bar{\varphi}^3 / (1 - \bar{\varphi})^2] (d^2 / \tau), \quad (13)$$

where  $\bar{\varphi}$  is the average porosity.

In general, the detailed reconstruction of the structural properties for the porous material can be performed by the methods of the percolation theory [15], deterministic or stochastic geometry [16].

## 6. The flow equations in the unsaturated porous material. The Leverett approach. The equilibrium condition with surrounding media

Under conditions of unsaturated plane flow in porous media [7], according to the previous definitions, we can introduce specific discharges of the liquid or gas phases as  $U_\alpha = \bar{\varphi} \eta_\alpha u_\alpha$ , where  $\alpha = \{l, g\}$  is the index of phase ( $u_\alpha = v_\alpha - v_s$  are superficial velocities of the  $\alpha$ -phases) and  $\eta_\alpha$  are corresponding pore saturations ( $\eta_l + \eta_g = 1$ ). In the case of stationary skeleton ( $v_s = 0$ ), the generalized Darcy laws by analogy with the relation (11) will take the form

$$U_\alpha = \bar{\varphi} \eta_\alpha v_\alpha = -(K_\alpha(\eta)/\rho_\alpha g) \partial p_\alpha / \partial x = -(k_s k_{r\alpha}(\eta)/\mu_\alpha) \partial p_\alpha / \partial x, \quad (14)$$

where  $k_{r\alpha}(\eta) = k_\alpha(\eta)/k_s$ ,  $\alpha = \{l, g\}$  are the relative permeability which satisfy the condition  $0 \leq k_{r\alpha}(\eta) \leq 1$  [14],  $k_\alpha(\eta) = K_\alpha(\eta)\mu_\alpha/\rho_\alpha g$ ,  $K_\alpha(\eta)$  are the absolute permeability and the hydraulic conductivity of  $\alpha$ -phase in the porous material, respectively.

Analyzing the generalized Darcy laws (11) and (14), we conclude that, according to the equation of a state  $p_\nu = f(T, x_\nu)$  ( $p_g = p_\nu/x_\nu$ ) [13] and the Young-Laplace (5) ( $p_l = p_g - p_c$ ) relation, the value of the main dependence  $p_c = f(\eta)$  is necessary for a successful description of diffusion processes of the liquid and gas phases in the porous material.

Let us assume that the porous skeleton is treated as aggregate of capillaries with the mean diameter  $d$ . Then in the relation (12)  $\psi = 4/d$  [5], where  $d = 4\sigma \cos \theta / p_c$ , and  $\theta$  is the angle of wetting between the liquid and gas phases in a capillary. Hence, similarly to the relation (13), it follows that

$$p_c \sqrt{k_s / \bar{\varphi}} / \sigma = \bar{\varphi} \cos \theta / [(1 - \bar{\varphi}) / \sqrt{\alpha_0 \tau}]. \quad (15)$$

Since  $\cos \theta$  is the function of the pore saturation  $\eta$  with liquid only, on the basis of (15) we will obtain the dimensionless  $J$ -Leverett function [7], which uniquely describes the process of liquid phase retention for the given structure of the porous material

$$J(\eta) = \sigma^{-1} p_c(\eta) / \sqrt{k_s / \bar{\varphi}}, \quad (16)$$

here  $\bar{\varphi}$  is the average porosity,  $k_s$  is the intrinsic permeability of porous skeleton,  $\sigma$  is the coefficient of surface tension.

It should be noted that an equilibrium state of liquid in porous media can be achieved under the condition that in the relation (14)  $U_l = U_g = 0$ . Such state is achieved for the equilibrium value of the material wetting  $\eta_{eqv}$ , which, according to relation (4), is determined on condition that  $p_l(\eta_{eqv}) = 0$ . Then we get  $p_c(\eta_{eqv}) = P_{amb}$ , where  $P_{amb}$  is the pressure of gas phase in the external environment.

## 7. Relative permeability of the liquid and gas phases according to the statistical model

To complete the analysis of the flow equations (11) and (14), we must determine the relations for the relative permeability of phases in porous material. In line with the statistical model [7], the following expressions have been proposed to calculate relative permeabilities for wetting (liquid)  $k_{rl}$  and non-wetting (gas)  $k_{rg}$  phases

$$k_{rl}(\eta) = \frac{\Theta^\kappa}{\alpha} \int_{r_{\min}}^r \Phi(r) dr, \quad k_{rg}(\eta) = \frac{(1 - \Theta)^\zeta}{\alpha} \int_r^{r_{\max}} \Phi(r) dr \quad \left( \alpha = \int_{r_{\min}}^{r_{\max}} r \Phi(r) dr \right), \quad (17)$$

where  $\Phi(r)$  is the function of pore size distribution according to the effective radius  $r$  (9),  $\Theta$  is the effective pore saturation (10) with liquid phase. Here  $\kappa$  and  $\zeta$  are the experimental parameters, which represent, respectively, the relation between the pore size and the curvature of path for flow of the particles of liquid and gas in an unsaturated porous material.

The relation (17) can be generalized for the case of random dependence  $p_c = f(\Theta(\eta))$ , where  $\Theta$  is the effective saturation, which corresponds to the real model for liquid phase retention in porous material. For this purpose from the relations (10) and (4) we obtain  $\Phi(r)dr = d\Theta$  and  $r = 2\sigma/p_c$ . So, changing the variables in the equation (17)  $r \rightarrow \Theta(\eta)$  in compliance with limits of the integration  $r_{\min} \rightarrow \Theta(\eta_{ir}) = 0$  and  $r_{\max} \rightarrow \Theta(\eta_{cr}) = 1$ , we obtain

$$k_{rl}(\Theta) = \frac{\Theta^{1/2}}{\beta} \int_0^{\Theta} [1/p_c(x)] dx, \quad k_{rg}(\Theta) = \frac{(1-\Theta)^{1/3}}{\beta} \int_{\Theta}^1 [1/p_c(x)] dx, \quad (18)$$

where  $\beta = \int_0^1 [1/p_c(x)] dx$  is the normalizing factor. According to the investigations of Mualem [17] and Luckner [18], in the expressions (17) there are given  $\kappa = 1/2$  and  $\zeta = 1/3$ .

## 8. A comparative analysis of models the moisture retention

At present, the most widely used means to describe the experimental dependence  $p_c = f(\eta)$  in the porous material are the semi-empirical approximations of Brooks–Corey [10] and van Genuchten [11]. Such approximations well agree with the data on the distribution function of the pore saturation  $\eta$  with liquid with respect to the mean radius  $r$  of meniscus for the finite volume of mesoscopic porous material (Fig. 2).

According to the Brooks-Corey model

$$\Theta = [1/\alpha p_c]^\lambda \quad (\alpha p_c \geq 1), \quad (19)$$

where  $\lambda$  is a dimensionless parameter that corresponds to the slope of the curve on the dependence  $\eta = f(r)$  at pore half-saturation with liquid  $\bar{\eta} = 1/2$ , this is reported in the work [7] to be the pore size distribution index,  $\alpha$  is the parameter to be determined

According to the van Genuchten model

$$\Theta = [1/(1 + (\alpha p_c)^m)]^n, \quad (20)$$

here  $m$  and  $n$  are empiric parameters.

Substituting the dependences  $p_c = p_c(\Theta)$ , which are defined by the expressions (19) and (20), into the relation (18) upon integrating, we obtain the following expressions for the relative permeability by the Brooks–Corey

$$k_{rl}(\Theta) = \Theta^{5/2+2/\lambda}, \quad k_{rg}(\Theta) = (1-\Theta)^{1/3} [1 - \Theta^{2(1+1/\lambda)}], \quad (21)$$

and the van Genuchten models

$$k_{rl}(\Theta) = \Theta^{1/2} [1 - (1-\Theta^{1/m})^m]^2, \quad k_{rg}(\Theta) = (1-\Theta)^{1/3} [1 - \Theta^{1/m}]^{2m}, \quad (22)$$

where  $m = 1 - 1/n$  is an integrability condition.

For  $\alpha \langle p_c \rangle \ll 1$ , the Brooks-Corey model (19) and the van Genuchen model (20) coincide, hence it follows that  $\lambda = mn = n - 1$ .

The empirical parameter  $m$  in the van Genuchen (20) model we obtain from the relation  $r \partial \eta / \partial r = -p_c \partial \eta / \partial p_c$  and the known experimental dependence  $\eta = f(r)$  (Fig. 2), when assume  $n = 1/(1 - m)$ . Then the pore size distribution function with respect to the effective radius (9) can be

described by the analytical expression

$$\Phi(r) = [m/(1-m)] \widehat{\Theta}(r)(1-\widehat{\Theta}(r))^{1/m}, \quad (23)$$

where  $\widehat{\Theta}(r) = \Theta(f(r))$  is the effective saturation of pores with liquid phase as the function of the effective radius  $r$  of meniscus.

It is expedient to introduce the parameter  $\alpha$  into the relations (19) and (20) at pore half-saturation with liquid ( $\bar{\eta} = 1/2$ ). Then, on the basis of the van Genuchten [11] model, we obtain

$$\alpha = \left(1/\bar{\theta}^{1/m} - 1\right)^{1-m} / \bar{p}_c = \bar{r} \left[ (\eta_{cr} - \eta_{ir}) / (\bar{\eta} - \eta_{ir})^{1/m} - 1 \right]^{1-m} / 2\sigma, \quad (24)$$

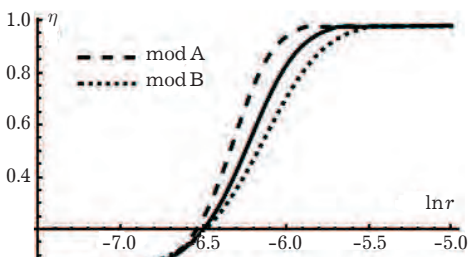
where  $\bar{p}_c = 2\sigma/\bar{r}$  is the capillary pressure, and  $\bar{r}$  is the mean radius of meniscus at pore half-saturation  $\bar{\eta}$  with liquid.

In line with the relation (19) and (24), within the framework of the Brooks-Corey [10] model, it is reasonably easy to see, using the actual dependence  $\eta = f(r)$  (Fig. 2) as an example, so that  $\alpha p_c = J(\eta)$  (16), where  $J(\eta) = [1/\Theta]^{(1-m)/m}$  is the  $J$ -Leverett function. Since  $1/\alpha = p_b$ , where  $p_b$  is the bubble pressure, the intrinsic permeability  $k_s$  of porous media is

$$k_s = \varphi \alpha^2 \sigma^2 = \varphi \sigma^2 / p_b^2, \quad (25)$$

here  $\varphi$  is the average porosity, and  $\sigma$  is the coefficient of surface tension.

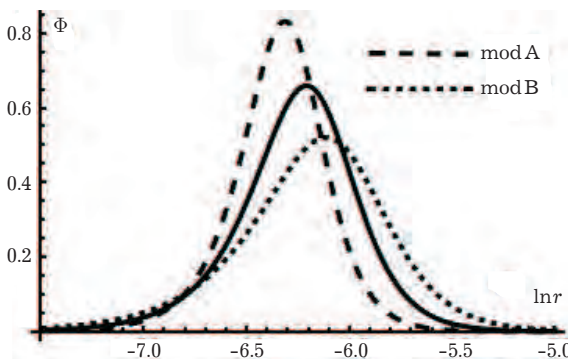
## 9. The results of numerical simulation



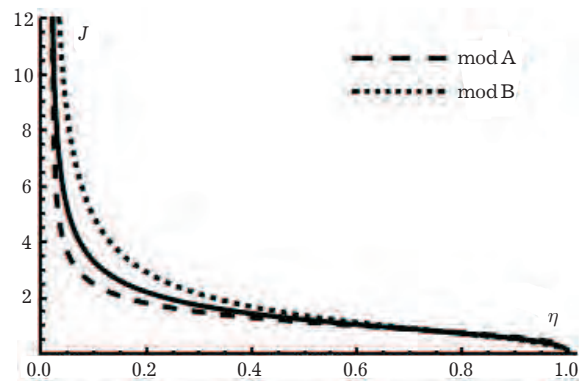
**Fig. 3.** The dependence of  $\eta = f(r)$  for the ceramic brick.

In Fig. 3, there is depicted the experimentally obtained dependences [19]  $\eta = f(r)$  for ceramic bricks from the district San Marco (Venice) ( $\varphi = 0.46$ ) in two modifications with respect to the average porosity  $\varphi$ : modA –  $\varphi = 0.4$  and modB –  $\varphi = 0.52$ .

Based on the given curves and relations (23) and (24), in line with the model description of van Genuchten (20), it has been found that for the basic material at  $\eta_{ir} = 0.015$  (Fig. 3) we have  $m = 0.67$  and  $p_b = 102.9$  kPa, while for the two modifications: modA ( $\eta_{ir} = 0.01$ ) –  $m = 0.72$  and  $p_b = 136.7$  kPa and modB ( $\eta_{ir} = 0.02$ ) –  $m = 0.61$  and  $p_b = 77.5$  kPa. According to the relations (16) and (25), as well as for the calculated model parameters  $m$  and  $\alpha$ , where taken  $\alpha = 1/p_b$  for the distribution function  $\Phi(r)$  (23) and  $J(\eta) = [1/\Theta(\eta)]^{1/m} - 1$  for the  $J$ -Leverett function (16), we obtain the dependences shown in Fig. 4 and Fig. 5, respectively.



**Fig. 4.** The normalized function of distribution the pore sizes by the effective radius.

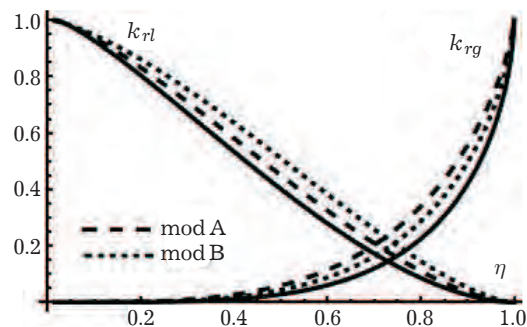


**Fig. 5.**  $J$ -Leverett function.



Fig. 6 depicts according to the relation (22) the relative permeability for the liquid  $k_{rl}$  and gas  $k_{rg}$  phases vs. the pore saturation  $\eta$  with liquid.

The values of the intrinsic permeabilities, defined by the relation (25) for the basic material  $k_s = 2.29 \times 10^{-13} \text{m}^2$  and for the two modifications:  $k_s = 1.13 \times 10^{-13} \text{m}^2$  (modA) and  $k_s = 4.57 \times 10^{-13} \text{m}^2$  (modB) give grounds to state that the values for equilibrium wetting of the porous material condition of static equilibrium ( $p_c(\eta_{eqv}) = P_{amb}$ , where  $P_{amb}$  is the pressure of gas phase in surrounding media under normal conditions), coincide with the peaks of the distribution function  $\Phi(r)$  (Fig. 4) and are equal to  $\eta_{eqv} = 0.64$  for the basic material ( $\varphi = 0.46$ ),  $\eta_{eqv} = 0.82$  for modA ( $\varphi = 0.4$ ) and  $\eta_{eqv} = 0.51$  for modB ( $\varphi = 0.52$ ), respectively.



**Fig. 6.** The relative permeability of liquid  $k_{rl}$  and gas  $k_{rg}$  phases.

## 10. Conclusions

The means of representation of the distribution function of pore size with respect to the effective radius under known drainage or sorption characteristics for the mesoscopic porous material have been described. The methods for determination of structural parameters in the semi empirical models of moisture retention have been demonstrated. Based on comparative analysis of these models, a simple formula to calculate the intrinsic permeability of porous skeleton has been obtained. According to the graphical analysis of the experimental data, it is established that with the increase of porosity (intrinsic permeability) of solid skeleton, the equilibrium wetting of porous material (pressure of bubbles) decreases. It is shown that the maximum of the distribution function is identical to the equilibrium wetting of porous material.

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## Дослідження структурних властивостей пористого матеріалу згідно з ізотермами сорбції або дренажних кривих

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У даній статті, відповідно до методу локального просторового усереднення, розглянуто основні співвідношення фізики поверхні і термодинаміки для опису процесів дифузії рідкої або газової фаз в неоднорідному пористому середовищі. Згідно з дренажними або сорбційними властивостями рідини у пористому скелеті означено нормовану функцію розподілу розміру пор за ефективним радіусом. Запропоновано співвідношення для визначення абсолютної і відносної проникності фаз у твердому скелеті. Проаналізовано залежність абсолютної проникності від структурних властивостей пористого матеріалу. Отримано просту умову рівноваги фаз у пористому скелеті з оточуючим середовищем.

**Ключові слова:** *пористі матеріали, адсорбція, капілярні явища, дифузія газу і рідини*

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