

Multiplicity of metastable nonergodic states of a dispersed nonwetting liquid in a disordered nanoporous medium

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Abstract. Three different metastable nonergodic states of a dispersed nonwetting liquid (water) in the Fluka 100 C8 and Fluka 100 C18 disordered porous media, as well as transitions between these states under variation of the temperature and the degree of filling, have been qualitatively described. It has been shown that the appearance of such states is due to spatial variations of the number of the nearest neighbors because of the broadening of the pore size distribution function $f(R)$, fluctuations of various local configurations of neighbors in the system of pores, and fluctuations of a configuration of a pore and its environment consisting of filled and empty pores on a percolation cluster. These states and transitions are caused by the competition between the effective repulsion of the nonwetting liquid from the wall of the pore, which is responsible for the “extrusion” of the liquid from the pore, and the effective collective multiparticle attraction of the liquid cluster in the pore to clusters in the neighboring connected pores. The theoretical dependences obtained make it possible to qualitatively describe experimental data.

1 Introduction

A stepwise transition from almost complete extrusion to complete entrapment at a small change in the degree of filling $\Delta\theta \sim 0.05$ near the critical value $\theta = 0.9$ (dispersion transition) was observed in a system consisting of a nonwetting liquid (water) and a disordered nanoporous medium (hydrophobized silica gel Libersorb 23 (L23)) [1]. This means that the nonwetting liquid transits to a “wetting” state at a certain degree of filling. The critical behavior of the system is also observed under variation of the temperature. With an increase in the temperature, complete entrapment changes to almost complete extrusion at $T_c \approx 293$ K. Systems of this type with strong nonlinear response to changing external conditions are interesting for fundamental science and applications. They can exhibit a nonergodic behavior [2] and can be used, e.g., for controlled release, for example, medicines under variation of the temperature, passive fire protection systems, and in materials with controlled penetrability for liquids or gases.

It was shown in reference [1] that a dispersed nonwetting liquid (water) in the disordered nanoporous medium L23 can be in two wetting states. According to [3], one of these states at temperatures above the critical value $T > T_c$ is due to the breaking of paths for the extrusion of the liquid at the decomposition of the infinite percolation cluster of filled pores. The other state of the dispersed liquid is metastable and is separated by a finite potential barrier from the state of the empty medium immersed in the liquid. In this work, these two states were

observed for another system consisting of the disordered nanoporous medium Fluka 100 C18 and water. For porous media Fluka 100 C8 and Fluka 100 C18, we also revealed another state of the dispersed liquid at $T < T_c$ for which the fraction of the dispersed liquid (θ_2) in the nanoporous medium is proportional to the degree of filling θ .

It is known [4–15] that the intrusion of a nonwetting liquid into a porous medium requires excess pressure, which can be estimated as the Laplace pressure. When the excess pressure vanishes, the non-wetting liquid should flow out of the porous medium. However, it is known that, for many porous media and liquids such as water, aqueous solutions of salts and organic materials, and liquid metals [4–11,16–18], a part of a liquid or the entire liquid after complete filling can remain in the porous medium after the removal of excess pressure. The entrapment of a nonwetting liquid during the experiment time was observed when studying the hysteresis of the intrusion-extrusion of the liquid in disordered porous media such as modified silica gels PEP300, PEP100, C8 (C18), C8W (Waters), KSK-G, Libersorb 23, Fluka 60 C8, and Fluka 100 C8 [4–8,10,15–18], as well as ordered porous zeolites, MCM-41, and porous glasses CPG and Vycor [10–14].

The volume fraction of the liquid remaining in the porous medium can be from 1% to 100% and this volume can remain unchanged in the observation time from several hours to several months for some systems [16]. However, the dependence of the volume of the liquid remaining in the porous medium on the observation time was revealed in other experiments [18]. According to [19,20], such systems can be considered as nonergodic.

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The entrapment of the nonwetting liquid was observed for disordered porous materials with various porosities, wide and narrow pore size distributions, and various surface energies of the liquid and interfaces between the liquid and the frame of the porous medium. The volume of the trapped liquid depends on the temperature [6].

The authors of [21,22] assumed that entrapment is due to the existence of configurations of pores that consist of, e.g., a large pore surrounded by smaller pores connecting with the large pore in a disordered porous medium. Then, after the filling of the porous medium and the subsequent reduction of excess pressure (for estimate, Laplace pressure), small pores become empty and the liquid cannot flow out of the large pore because possible paths for its flow are broken. An increase in the volume of the liquid (mercury) trapped in a silica gel with an increase in the size of granules is attributed to the existence of such configurations of neighboring pores [21,22]. The authors of [21,23] introduced a lattice Hamiltonian, which contains two sets of the occupation numbers, to describe the intrusion-extrusion hysteresis and entrapment after the complete filling. One set describes the occupation of a site of the lattice by either a pore or a frame. The other set corresponds to an empty or liquid-filled pore. In the performed Monte Carlo studies of entrapment with the Glauber-Kawasaki algorithm, it was also assumed that the liquid flows from a filled pore to a neighboring empty pore through vapor transport. The performed calculations qualitatively describe the observed increase in the volume of mercury trapped in pores for CPG and Vycor glasses with the reduction of the experiment time. However, it is noteworthy that the assumption made in references [21,23] of transport through gas diffusion contradicts the observed liquid extrusion rate after the removal of excess pressure in the experiments with water and the L23 porous medium [24].

The stepwise dependence of the fraction of the liquid trapped in the porous medium on the degree of filling revealed in reference [1] means that this phenomenon is associated with the interaction between liquid clusters in neighboring pores. The surface energy of two clusters in connected neighboring pores is lower than the surface energy of two clusters separated by empty pores by the surface energy of the liquid-gas interface absent in the mouth of the throat connecting the neighboring filled pores. The decrease in the surface energy of two liquid clusters in neighboring pores can be treated as the negative energy of their interaction, i.e., as the effective “attraction” between clusters, which can result in their “condensation” and the appearance of a metastable state of a liquid in a disordered nanoporous medium. Consequently, possible explanation of the dependence of the degree of entrapment of the liquid in the disordered porous medium on the degree of filling can be found by rejecting assumptions of intrusion-extrusion in individual “noninteracting” pores according to the Laplace equation and various its modifications [10,21,25,26]. For this reason, it can be thought that the existence of the critical degree of filling and the critical temperature means that liquid clusters in neigh-

boring pores exhibit collective properties characteristic of strongly interacting systems of particles. The inclusion of the correlation interaction between liquid clusters allows the description of thermal effects and temperature dependence of the pressure of intrusion and extrusion of the nonwetting liquid in the disordered porous medium [27].

A model for the description of the dispersion transition in the disordered porous medium with a narrow pore size distribution was proposed in references [2,3]. In this model, the entrapment of the liquid in the porous medium is due either to the breaking of extrusion paths or to the dependence on the temperature and the degree of filling of the average potential barrier for extrusion. States appearing because of the breaking of the infinite cluster can be considered as nonergodic because they are separated from the ground state by an infinite potential barrier within the considered extrusion model through the system of filled pores. States with a finite potential barrier are metastable and (or) quasi-nonergodic [28]. The height of this barrier is determined by the multiparticle interaction between liquid clusters in neighboring pores that is averaged over variations of configurations of filled and empty pores with various sizes in the space of the disordered medium. This barrier is equal to the difference between the energy of the multiparticle interaction between liquid clusters in the configuration and the energy of the interaction of a cluster with the frame of the medium in pores on the shell of the infinite percolation cluster of filled pores. The equality of these energies is a condition of the spontaneous extrusion of the liquid from the nanoporous medium. This approach makes it possible to calculate, within the analytical percolation theory, and to describe the experimental dependences of the fraction of the trapped liquid θ_2 on the degree of filling θ_1 and the temperature T for the L23-water system.

However, significantly different dependences of the volume of the trapped liquid on the degree of filling θ_1 are discussed in this work for systems consisting of distilled water and hydrophobized silica gels Fluka 100 C8 and Fluka 100 C18 close in parameters (Sect. 2). In particular, the stepwise dependence of the fraction of the trapped liquid θ_2 on the degree of filling θ_1 is not observed for the Fluka 100 C8-water system in the temperature range under study. In contrast to the L23-water system, a new state of the trapped liquid that is characterized by a linear increase in θ_2 with an increase in the degree of filling θ_1 was observed. The Fluka 100 C18-water system has two critical temperatures $T_{c1} \approx 330$ K and $T_{c2} \approx 340$ K. Above T_{c1} , a transition occurs from the state of the system in which $\theta_2 \sim \theta_1$ to the state in which the dispersion transition occurs at $\theta_1 = \theta_c \approx 0.5$ ($T \approx 330$ K). Above T_{c2} , this state changes to the state of small entrapment independent of the temperature and the degree of filling θ_1 . This behavior qualitatively differs from the behavior of the previously studied L23-water system [1].

Although the behaviors of all three systems under study are significantly different, these observed effects can be qualitatively described with allowance for features of the multiparticle interaction between liquid clusters in the

disordered nanoporous medium with a wide pore size distribution and percolation nature of extrusion (Sect. 3).

To describe three different observed states of the non-wetting liquid in disordered porous media under study, a wide pore size distribution characteristic of them should be taken into account within the theory developed in reference [2]. The wide distribution requires the inclusion of the main property of a disordered nanoporous medium, i.e., spatial variations of the number of nearest neighbors. As a result, not only the distribution of pores over sizes and variations of the number of neighbors of filled and empty pores on the shell of the percolation cluster, but also variations (fluctuations) of the number of neighbors around a filled pore in the space of the porous medium were taken into account when calculating the averaged potential barrier for extrusion.

The volume of the trapped liquid at an arbitrary degree of filling was calculated within the analytical percolation theory for the ground state of the system with the infinite percolation cluster of filled pores in the disordered porous medium with the connected structure of pores. In this state, extrusion from any pore belonging to the infinite percolation cluster of filled pores is ensured (Sect. 3). States of the nonwetting liquid, which is dispersed in the disordered porous medium, are related within the proposed model to the properties of disordered media such as pore size distributions, local configurations of pores in the porous medium and their characteristics such as the number of nearest neighbors because of the wide pore size distribution (Sect. 3). The volume of the trapped liquid independent of the degree of filling at the “break” of extrusion paths is calculated in Section 3. The resulting qualitative dependences are compared to experimental data.

2 The data under study

2.1 Materials and methods

The entrapment of the nonwetting liquid, distilled water, was observed in the experiments with two disordered nanoporous media Fluka 100 C8 and Fluka 100 C18. These hydrophobized media have the same material of the frame and are produced by Sigma-Aldrich. The Fluka 100 C8 medium was obtained in one of two produced variants and it is Silica gel 100 C₈, Reversed phase # 60759-50G (Sigma-Aldrich), whose surface is modified with 8-alkylsilane. The Fluka 100 C18 medium (Silica gel 100 C₁₈ – Reversed phase # 60756-50G, Sigma-Aldrich) is modified with 18-alkylsilane.

The characteristics of the porous media: specific volume of pores V_p , average radius $\langle R \rangle$, and porosity (φ) are briefly presented in Table 1. Also in Table 1 characteristics of the L23 silica gel similarly hydrophobized and previously studied in reference [1] are included. According to Table 1, Fluka 100 C8 and Fluka 100 C18 have the same average radius of pores, but volume of pores, and porosity for the Fluka 100 C18 medium are smaller than the respective quantities for Fluka 100 C8. The porosity (φ) of these media is smaller than that for L23.

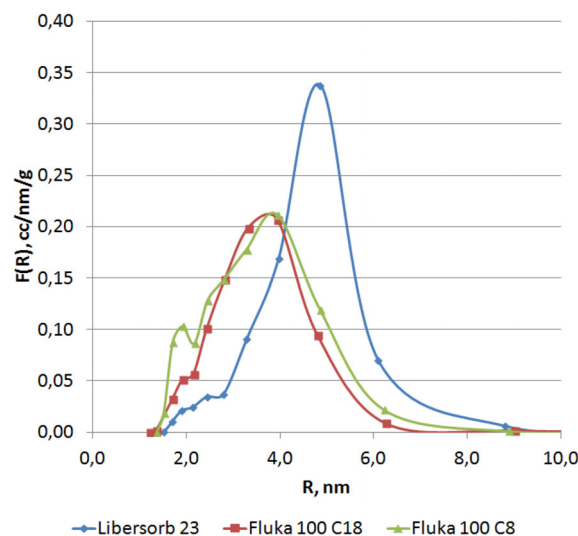


Fig. 1. Pore size distributions for three nanoporous media under investigation obtained by the BJH method.

Table 1. Characteristics of porous media.

	Fluka 100 C8	Fluka 100 C18	L23
V_p , cm ³ /g	0.56 ± 0.02	0.46 ± 0.02	0.66 ± 0.02
$\langle R \rangle$, nm	3.9 ± 0.2	3.9 ± 0.2	4.9 ± 0.2
φ	0.49 ± 0.02	0.42 ± 0.02	0.66 ± 0.02

The pore size distribution functions $f(R)$ for the porous media, determined from nitrogen desorption isotherms by the BJH method [29,30], are shown in Figure 1 in comparison with the narrower pore distribution for the L23 medium. According to [29], the dependences $f(R)$ shown in Figure 1 can be discussed as those providing only a qualitative representation of these distributions. Within this approach, according to Figure 1, both media under study have the same average radius corresponding to the maximum of the distribution function, whereas the number of pores with sizes R $\langle R \rangle$ and smaller for the Fluka 100 C8 medium is slightly larger than that for Fluka 100 C18. According to [31–33], this qualitative difference between the distribution functions can be attributed to the different lengths of the modifier molecules of alkylsilane and, as a result, to a larger blocking of small pores by long molecules (C18) and to a close, but larger relative number of large pores. As will be shown in Section 3, the mentioned differences between the parameters of the porous media under study make it possible to propose an explanation of the properties of various detected “wetting” states of the dispersed liquid in the Fluka 100 C8 and Fluka 100 C18 media.

In our experiments, it was determined the dependence of the volume fraction of pores filled with the trapped liquid on the volume fraction of pores previously filled with the liquid. The method of study was similar to the method used in mercury [29] or water [5,26] porometry and more detailed measurement procedure and high-pressure bench was described in references [1,5].

2.2 Results

Figure 2 shows the dependences of the volume fraction of pores θ_2 filled with the trapped liquid on the degree θ_1 of preliminary filling of pores in the (a) – (Fluka 100 C8-water) system at temperatures of 293, 313, and 333 K and (b) – (Fluka 100 C18-water) system at temperatures of 293, 303, 313, 323, 333, and 343 K. As can be seen in Figure 2a, the volume fraction of pores filled with the trapped liquid increases linearly with the degree of filling. At temperatures of 293 and 313 K, the amount of the trapped liquid is equal within the measurement error to the amount of the liquid intruded into pores. An increase in the temperature to 333 K does not change the linear dependence $\theta_2(\theta_1)$, but a tendency to a decrease in the volume of the trapped liquid can be seen.

The dependences $\theta_2(\theta_1)$ for the (Fluka 100 C18-water) system are shown in Figure 2b for six temperatures 293, 303, 313, 323, 333, and 343 K. The dependences $\theta_2(\theta_1)$ for the temperatures of 293, 303, and 313 K are linear within the measurement error and are similar to those obtained for the (Fluka 100 C8-water) system. An increase in the temperature from 313 to 323 K changes this dependence from linear at 313 K to “stepwise” at 323 K. At the latter temperature, the volume fraction of pores filled with the trapped liquid changes stepwise at the degree of preliminary filling $\theta_1 = \theta_{cr} \approx 0.63$. The same singularity is observed in the dependence $\theta_2(\theta_1)$ at $T = 333$ K. An increase in the temperature from 323 K to 333 K results in an increase in the critical degree of filling θ_{cr} from 0.63 to 0.73. With a further increase in the temperature by 10 K to 343 K, another change in the shape of the dependence $\theta_2(\theta_1)$ is observed. The quantity θ_2 becomes practically independent of the degree of filling and is $\theta_2 \approx 0.1$ within the measurement error.

Thus, the (Fluka 100 C8-water) system in the temperature range under study exhibits one state of the trapped nonwetting liquid for which the linear law $\theta_2 = c\theta_1$ ($c = \text{const.}(T)$) is valid throughout the entire range of the degree of filling of the disordered porous medium with the liquid. The (Fluka 100 C18-water) system in the same temperature range exhibits three different states of the dispersed liquid. One of them at low temperatures $T < 323$ K is similar to that found for the (Fluka 100 C8-water) system. The dispersed liquid in this system transits to the second state at a temperature of $T = 323$ K and the degree of filling $\theta_1 = \theta_{cr} \approx 0.63$. At smaller degrees of filling $\theta_1 < \theta_{cr}$, the linear law $\theta_2 = c\theta_1$ changes to the law $\theta_2 = \text{const.}$ in the temperature range where this state is observed. The third state of the dispersed liquid was observed at $T > T_{cr} \approx 338$ K. The volume of the trapped liquid in this state is independent of the degree of initial filling of pores for all θ_1 values under study. The second and third states of the dispersed liquid trapped in the disordered porous medium were previously revealed in the experiments with the (L23-water) system [1].

For comparison, Figure 3 shows the dependences $\theta_2(\theta_1)$ for the (Fluka 100 C18-water) and (L23-water) systems at the temperatures of 333 and 286 K, respectively. It can be seen that the volume fraction of pores in these

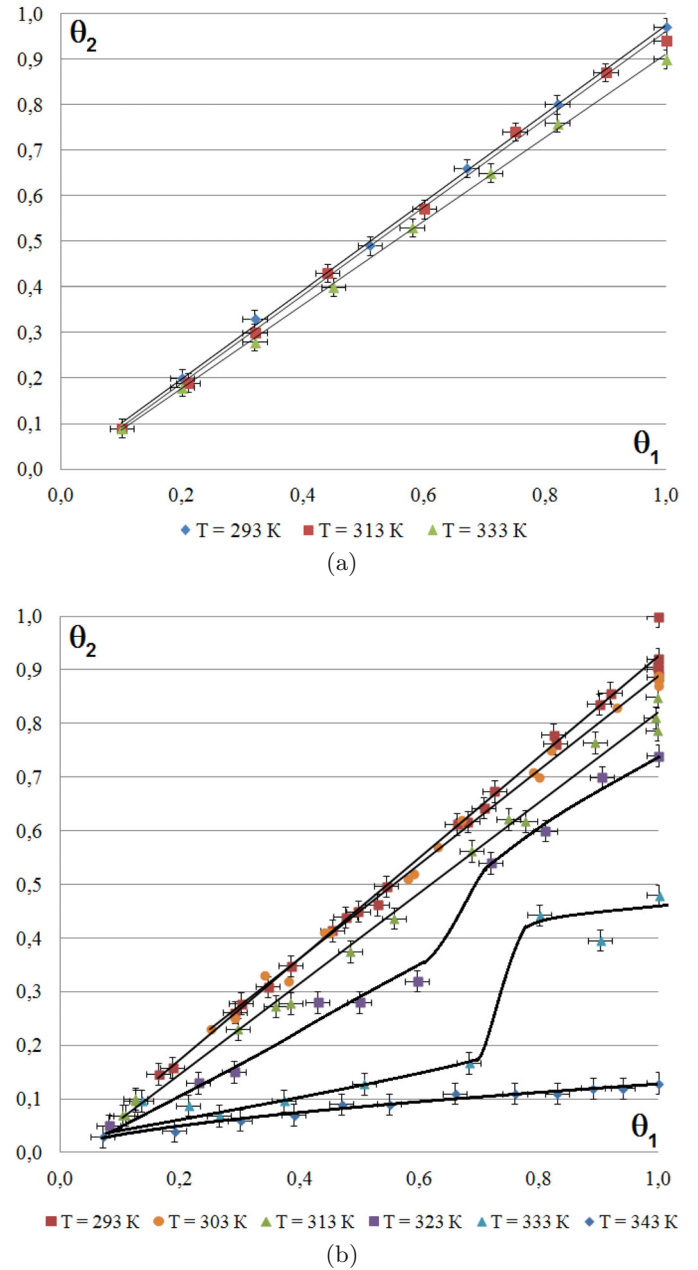


Fig. 2. Dependence $\theta_2(\theta_1)$ for the (a) (Fluka 100 C8-water) system at temperatures of 293, 313, and 333 K; (b) (Fluka 100 C18-water) system at temperatures of 293, 303, 313, 323, 333, and 343 K. Points – experimental data. The solid lines are trends of the dependences.

systems at respective temperatures changes stepwise. This indicates the appearance of the second described state in these systems.

According to the pore size distribution functions $F(R)$ shown in Figure 1, the radius $\langle R \rangle$ corresponding to the maximum of the distribution function is the same for both Fluka 100 C8 and Fluka 100 C18 media, whereas the pore size distribution for the former medium is wider than that for the latter medium. The FWHM of the distribution is $\delta R/R \sim 0.9$ for Fluka 100 C8 and is $\delta R/R \sim 0.75$

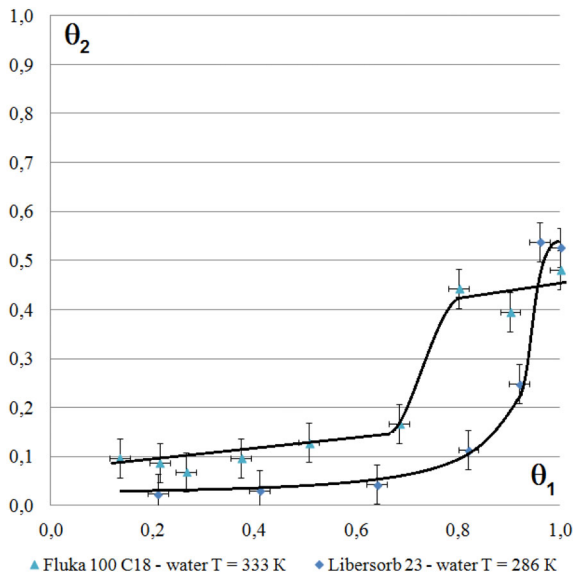


Fig. 3. Dependences $\theta_2(\theta_1)$ in the (Fluka 100 C18-water) and (Libersorb 23-water) systems. Points – experimental data. The solid lines are trends of the dependences.

for Fluka 100 C18. The most probable radius $\langle R \rangle$ for the L23 medium is larger and the FWHM of the distribution $\delta R/R \sim 0.3$ is several times smaller than the respective values for the Fluka 100 C8 and Fluka 100 C18 media. These qualitative differences in the parameters of the porous media under study, as will be shown in Section 3, make it possible to propose the explanation of the properties of the detected different “wetting” states of the liquid dispersed in media.

3 Discussion of the experimental data

A model that provides the explanation of the dispersion transition experimentally detected in reference [1] in a narrow range of the degree of filling θ and in a narrow temperature interval when the nonwetting liquid becomes “wetting” was developed in references [2,3]. The proposed description of this phenomenon is based on analytical methods of percolation theory and the inclusion of the “multiparticle interaction” of a liquid cluster in a filled pore with liquid clusters in neighboring pores. The transition of some nanoclusters of the nonwetting liquid to the “wetting” state is associated with a decrease in the surface free energy owing to the collective interaction between liquid clusters. To describe the dispersion transition in the L23 porous medium with the narrow pore distribution with the relative width $\frac{\Delta R}{R} \sim 0.3$, it was assumed in reference [3] that $\frac{\Delta R}{R} \ll 1$. At the same time, porous media studied in this work have a wide pore size distribution with the relative width $\frac{\Delta R}{R} \sim 1$ (Fig. 1). For this reason, the model developed in references [2,3] was generalized to the case of wide pore size distributions. This allows the explanation of the several wetting states of the nonwetting liquid in the porous medium observed in this work.

3.1 Physical picture of transitions of the nonwetting liquid to a dispersed state of the disordered porous medium with a wide pore size distribution

We consider a porous medium formed by a rigid frame inside which pores constitute the spatial structure of overlapping spheres with various sizes. This model of the porous medium is a generalization of the model of randomly distributed spheres that is widely used to describe porous media [34]. In the model of randomly distributed spheres, a unit pore is a spherical void with cuts (throats). In this model, a “quantum” of the change in the volume of the liquid in the medium at intrusion (extrusion) is intrusion-extrusion for one pore. It is suggested that the volume of throats is negligibly small as compared to the volume of pores. When the liquid is intruded into a pore and is extruded from it, menisci of the liquid are formed in these throats. Pores can be filled only when they are connected to each other through throats and to the surface of the porous medium. This is the case if the porosity of the medium is such that the system of pores in it is above the percolation threshold $\varphi > \varphi_c$. For various models of the porous medium, the percolation threshold is $\varphi_c = 0.16 \div 0.3$ [35,36] and is characteristic of the porous medium. The interconnection of pores is a result of the appearance of an infinite (geometric) cluster consisting of such pores at $\varphi = \varphi_c$. At a given pressure, only pores whose radii are larger than a certain value can be filled; therefore, the filling of the disordered porous medium at $\varphi > \varphi_c$ is the filling of the percolation cluster consisting of interconnected pores with various radii.

The extrusion of the liquid from a pore becomes possible under the following two conditions.

- (i) Its extrusion should be energetically favorable. Negative work should be spent on the extrusion of the liquid from the pore owing to the change in the energy of the (porous medium-liquid) interface and to the formation of menisci in the throats of neighboring pores.
- (ii) Since the liquid can flow only through a connected system of filled pores, geometric paths for the extrusion of the liquid from a given pore should exist.

For this reason, the extrusion of the liquid from the pore in this medium at the reduction of excess pressure can be considered as the depletion of the pore belonging to the percolation cluster of connected pores with various sizes filled with the liquid.

We consider a change in the state of the (liquid-porous medium) system at the extrusion of the liquid from the pore surrounded by empty and filled pores at partial filling. These surrounding pores are connected to the pore under consideration through throats in the mouths of which a meniscus appears if one of two connected pores is not filled with the liquid. According to the statistical theory of fluctuations [37], the probability w of the change in the state of the system in unit time at the extrusion of the liquid from the pore under consideration under the action of fluctuations in the system is given by the expression $w \sim \exp(\Delta S)$, where ΔS is the change in the entropy

of the system ΔS at the extrusion of the liquid from the pore. We suggest that the change in the temperature of the system can be neglected in this process. This corresponds to the experimentally observed small thermal effect [38]. Then, the probability can be written in the form

$$w = w_0 \exp(-\delta A/T). \quad (1)$$

Here, w_0 is the pre-exponential factor taking into account the extrusion dynamics of the liquid from the porous medium and δA is the isothermal work that should be spent on the extrusion of the liquid from the pore. This work serves as a potential barrier for extrusion in the case under consideration. According to equation (1), the entrapment of the liquid in this medium can be due, first, to the geometric reason, when the porous medium contains clusters with a finite number of filled pores for which paths for extrusion are absent (see Fig. 4) and, second, to the energy reason associated with the change ΔS . The quantity δA in equation (1) should include the work pV done by the system for an increase in its volume by the volume V of the pore at the pressure p and the change in the surface energy ΔE of the liquid in the pore. In the initial state, the surface energy E_i of the liquid in the pore consists of the energy E_{isl} of the (solid (frame)-liquid) interface and the surface energy E_{ilg} of the liquid-gas interface summed in all mouths of the throats connecting the pore under consideration with surrounding empty pores. We assume that the state of the liquid in surrounding pores remains unchanged at the extrusion of the liquid from the pore under consideration. Consequently, the surface energy E_f in the final state consists of the energy E_{fsg} of the solid-gas interface and the energy E_{flg} of the liquid-gas interface, which appears in the mouths of the throats connecting the empty pore under consideration with the surrounding filled pores. We represent the work δA spent on an increase in the volume of the system and on the change in the surface energy in the form of the difference between the energy of the interface in the pore near the surface of the frame and the difference between the total surface energy of menisci in the mouths of all throats connecting the pore with the neighboring pores in the final and initial states after and before extrusion. In this case,

$$\begin{aligned} \delta A &= pV + \Delta E, & \Delta E &= \Delta E_s + \Delta E_l \\ \Delta E_s &= E_{fsg} - E_{isl}, & \Delta E_l &= E_{flg} - E_{ilg}. \end{aligned} \quad (2)$$

The local characteristics of the disordered porous medium at intrusion-extrusion of the liquid change randomly because of various spatially inhomogeneous geometric configurations of pores and their environment.

Figure 4 shows the schematic of a change in the state of a fragment of the disordered porous medium and the number of menisci in the pore (a), (c), (e) before and (b), (d), (f) after its depletion at various degrees of filling. Filled and empty pores are given in black and white, respectively, and the frame of the porous medium is shaded. The arrows in Figures 4a–4d indicate menisci and their number. It can be seen in Figures 4a and 4b that the extrusion of the liquid from a pore in the completely filled

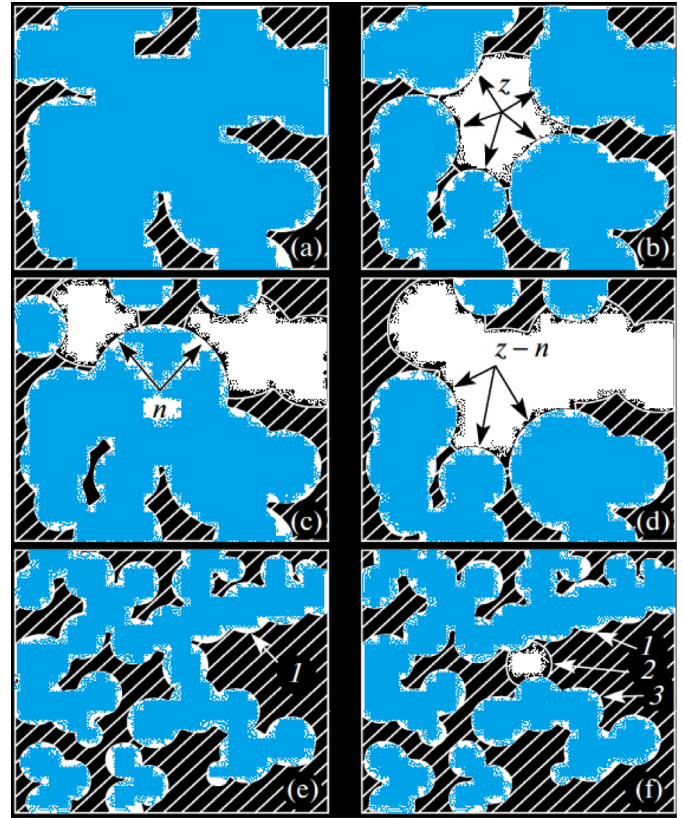


Fig. 4. Schematic of the change in the state of the porous medium and the number of menisci for a pore before and after the depletion of the pore at the degree of filling of the porous medium (a, b) $\theta_1 = 1$ and (c, d) $\theta_1 < 1$; (e, f) schematic of the cluster of filled pores 3 in the absence of paths for the extrusion of the liquid; z is the number of nearest neighbors; and n is the number of menisci for the pore filled with the liquid in the partially filled porous medium.

porous medium ($\theta_1 = 1$, Fig. 4a) is accompanied by the formation of menisci whose number is equal to the number of nearest neighbors z (Fig. 4b) of this pore. If the degree of filling is $\theta_1 < 1$, the initial number of menisci n (Fig. 4c) after the extrusion of the liquid from the pore changes to $z - n$ (Fig. 4d). Figure 4f shows the formed cluster of filled pores 3 from which extrusion is impossible because the connection with the infinite cluster of filled pores 1 is broken after the extrusion of the liquid from the pore 2.

Spatial inhomogeneity is responsible for the formation of various configurations of empty and filled pores in the disordered porous medium.

Let z be the number of neighboring pores for a given pore before extrusion including n filled pores and $z - n$ empty pores (see Fig. 4); therefore, the number of menisci in the mouths of throats is $z - n$. After extrusion, the number of menisci becomes equal to the number n of filled neighboring pores. The number of menisci n depends on the configuration of the pore and its environment. Let W be the difference between the numbers of menisci after and before the extrusion of the liquid from the pore divided by the number of nearest neighbors and averaged over all

local configurations:

$$W = \left\langle \frac{2n - z}{z} \right\rangle_{conf}. \quad (3)$$

Here, $\langle \dots \rangle_{conf}$ means averaging over all local configurations of the pore and its environment. Then, the quantities ΔE_s and ΔE_l are given by the expressions

$$\begin{aligned} \Delta E_s &= (\sigma_{sg} - \sigma_{sl})(s - S_m) = -\delta\sigma(s - S_m), \\ \Delta E_l &= \sigma \langle s_m(n - (z - n)) \rangle_{conf} \\ &= \sigma S_m \left\langle \frac{(2n - z)}{z} \right\rangle_{conf} = \sigma S_m W. \end{aligned} \quad (4)$$

Here, $\delta\sigma = |\sigma_{sg} - \sigma_{sl}|$ is the change in the specific energy of the surface of a solid (frame of the porous medium) at the extrusion of the liquid. For the nonwetting liquid, $\sigma_{sg} < \sigma_{sl}$; s , S_m , and $s_m = \frac{S_m}{z}$ is the area of the surface of pores, the area of the surface of menisci in the mouths of throats of pores, and the area of the surface of one meniscus, respectively; obviously, $S_m < s$.

According to equations (2) and (4), the potential barrier for extrusion decreases with a decrease in the pressure p . The fraction of the trapped liquid in the described experiments were determined after the removal of excess pressure, i.e., at $p = 0$. In this case, the potential barrier $\delta A(p = 0)$ is the sum $\Delta E_s + \Delta E_l$; since $\sigma_{sg} < \sigma_{sl}$ and $S_m < s$, $\Delta E_s < 0$ and ΔE_l changes sign when the average relative number of filled neighboring pores is $\langle \frac{n}{z} \rangle_{conf} = 1/2$. At $\langle \frac{n}{z} \rangle_{conf} < 1/2$ and, according to equation (3), at $\Delta E_l < 0$, the potential barrier for extrusion is negative and the nonwetting liquid flows out of the porous medium after the removal of excess pressure. If the average relative number of filled neighboring pores is larger than half, $\langle \frac{n}{z} \rangle_{conf} > 1/2$, the potential barrier for extrusion can be both positive and negative, depending on the relation between ΔE_s and ΔE_l . Thus, the dispersed state of the nonwetting liquid in the porous medium at $p = 0$ is possible if the change in the energy ΔE_l of the liquid in the mouths of throats connecting the pore with neighbors at extrusion is larger than the change in the energy $|\Delta E_s|$ of the wall boundary of the frame in the pore.

At $\delta A = 0$, the spontaneous extrusion of the nonwetting liquid should occur under the action of thermal fluctuations in the system. This condition can be used to estimate the critical degree of filling θ_{cr} above which the state appears in which the nonwetting liquid can remain in the porous medium at excess pressure $p = 0$.

The degree of filling θ_1 in the mean field approximation is the fraction of filled pores in the macroscopically small volume of the porous medium. In this approximation, under the assumption that all local configurations appear with the same probability, the critical average fraction $\langle \frac{n}{z} \rangle_{conf}$ of filled neighboring pores for the pore under consideration can be estimated as $\langle \frac{n}{z} \rangle_{conf} \approx \theta_{cr}$, and the condition $\delta A(p = 0) \approx 0$ with allowance for equation (3) can be represented in the form

$$\delta\sigma \left(1 - \frac{z s_m}{s}\right) = \sigma \frac{z s_m}{s} (2\theta_{cr} - 1). \quad (5)$$

We introduce the cosine of the wetting angle, $|\cos \psi| = \delta\sigma/\sigma$, and the parameter $\eta = \frac{z s_m}{s}$ determining the geometric connectivity of pores through the mouths of neighboring pores. To estimate the number of neighboring pores in the disordered porous medium, we use the model of randomly distributed overlapping spheres [34,39]. In this model, pores are represented in the form of randomly distributed overlapping spheres with the same radius R . The area s_m of the mouths of the throats connecting two neighboring pores and the average number z of the nearest neighbor pores in this model depend on the porosity φ and are given by the formulas [34,39]

$$z = -8 \ln(1 - \varphi), \quad s_m = \frac{9\pi^2}{256} R^2. \quad (6)$$

Condition (4) for the critical degree of filling can be written in the form

$$\theta_{cr} = \frac{1}{2} \left(1 + |\cos \psi| \left(\frac{1 - \eta}{\eta}\right)\right). \quad (7)$$

The porosity of the system under study is $\varphi \approx 0.5$ and, according to equations (6), the number of the nearest neighbors is $z = 7$ and the area of the mouths of pores is $s_m = 13 \text{ nm}^2$. Using the method developed in reference [27], we obtain $|\cos \psi| \approx 0.1$. Then, according to equation (7), the critical degree of filling at which the nonwetting liquid can be trapped in the porous medium at zero excess pressure is $\theta_{cr} = 0.6$. This value is consistent with the value $\theta_{cr} \sim 0.65$ experimentally observed at $T = 333 \text{ K}$ (see Sect. 2).

According to equations (2)–(4), the potential barrier at degrees of filling smaller than θ_{cr} is negative, $\delta A(p = 0) < 0$, and the characteristic extrusion time $\tau \sim w^{-1}$ is determined by the hydrodynamic time $\tau_0 \sim w_0^{-1}$ of the motion of the liquid in the porous medium. The quantity τ_0 was determined experimentally for the systems studied in reference [40] on the intrusion-extrusion dynamic at almost zero excess pressure and is $\tau \approx 10^{-1} \text{ s}$. The characteristic potential barrier for the states studied in this work at the extrusion observation time $t_{exp} \sim 10^3 \text{ s}$ is no less than $\delta A \approx 0.4 \text{ eV}$.

We now discuss a physical reason for the appearance and destruction of a metastable dispersed state of the liquid at entrapment. The surface energy of the system of liquid clusters in completely filled pores is not reduced to the sum of the surface energies of all independent liquid clusters. Clusters can contact with each other in neighboring pores connected through throats. The mouths of these throats are free of the liquid-gas interface if the pore is connected through throats with neighboring filled pores. This means that the surface energy of two clusters in neighboring pores is lower than the surface energy of two independent clusters by the energy of the liquid-gas interface in the mouth of the throat connecting these filled pores. A decrease in the surface energy can be considered as the negative energy of the interaction between two liquid clusters, i.e., as the effective attraction between interacting clusters. This is the physical meaning of the energy ΔE_l introduced in equations (2) and (3). It takes

into account the “multiparticle interaction” of the liquid cluster in the pore with clusters existing in neighboring connected pores. The interaction between the liquid clusters can be responsible for the situation where the total energy of the “multiparticle attractive interaction” at the degree of filling $\theta > \theta_{cr}$ becomes higher (see Eq. (4)) than the energy of the liquid-solid interface. In this case, extrusion is energetically unfavorable after the removal of excess pressure. The probability of extrusion w (1) can be smaller than the inverse observation time and the system of clusters becomes “condensed”. With an increase in the temperature, σ decreases, whereas $\delta\sigma$ and $|\cos\psi|$ increase. For this reason, above a certain critical temperature $T > T_{cr}$, the total energy of the “multiparticle attraction” becomes lower (see Eq. (4)) than the energy of the liquid-solid interface. In this case, the “condensed” state of the system of clusters is destroyed and the liquid flows out of the porous medium. The above analysis and estimates of θ_{cr} show that the appearance of the state of the dispersed nonwetting liquid in the porous medium at $\theta > \theta_{cr}$ and its destruction can be attributed to the formation of a potential barrier because of the change in the number of menisci in the mouths of throats connecting neighboring filled pores and the pore from which the liquid flows at a temperature above the critical temperature $T > T_{cr}$.

The above estimates show that, at these degrees of filling and the extrusion observation time smaller than the fluctuation decay time of the “condensed” state of the system, a metastable state of the nonwetting liquid appears in the form of the ensemble of liquid nanoclusters in pores (dispersed liquid).

The simplified qualitative explanation of the observed (see Fig. 3) stepwise change in the volume fraction of pores filled with the trapped liquid as a function of the degree of filling near $\theta_{cr} \sim 0.65$ for the (Fluka 100 C18-water) system was given above. However, the states of small entrapment of the liquid in the system observed for any degree of filling at increased temperatures ($T > 343$ K) require additional discussion. The possibility of the appearance of states in which the dependences of the volume fraction of pores filled with the trapped liquid on the degree of filling $\theta_2(\theta_1)$ are linear for the (Fluka 100 C8-water) and (Fluka 100 C18-water) systems, as well as the change of this dependence from linear at 313 K to “stepwise” at $T = 323$ K for the (Fluka 100 C18-water) system, should also be additionally analyzed.

The above estimates were based on the assumptions that the disordered porous medium is homogeneous and isotropic and that the local geometric configuration consisting of the liquid cluster in the completely filled pore and its nearest environment of liquid clusters in connected neighboring pores is identical throughout the volume of the porous medium. However, there are several reasons for which various spatially inhomogeneous geometric configurations consisting of the liquid cluster in the pore and its environment appear in the disordered porous medium. Such an inhomogeneity can appear according to the model of randomly distributed overlapping spheres at $R = \text{const.}$ [34,39] in the case of spatially

nonuniform porosity. According to equation (5), the number of the nearest neighbor pores and, as a result, variation of the potential barrier and the probability of extrusion of the liquid from the pore are inhomogeneous in this case. Another reason can be the dependence of the connectivity factor η of the pores (see Eq. (6)) on the radius of the pore if the porous medium contains pores with different sizes. In this case, for example, a larger pore can be surrounded by smaller pores or by a smaller number of neighboring pores. The probability of the appearance of such local configurations is larger for wide pore size distributions; consequently, the effect of these configurations can be significant for such distributions. As a result, spatial variations appear in geometric configurations of the pore and its environment. This situation appears at various initial degrees of filling because larger pores are filled at smaller degrees of filling requiring lower pressures.

An additional reason for the variation of the local configuration of the pore and its environment [36] is associated with the fractal structure of the percolation cluster of filled pores, which has a nonsmooth strongly rough shell [36]. Because of the roughness of the shell of the percolation cluster, significant variations of the number of filled and unfilled pores appear near each pore on the shell of the percolation cluster; as a result, the local configuration of the pore and its environment and, according to equation (4), the potential barrier for extrusion are varied. Thus, variations of the local configurations of the pore and its environment can be taken into account within the percolation theory and the extrusion of the liquid from the porous medium can be adequately described. Variations of the local configurations of the pore and its environment at the extrusion of the liquid from the porous medium can result in the breaking of the infinite cluster of filled pores and in the formation of clusters containing a finite number of filled pores for which paths for extrusion are absent.

As was mentioned above, disordered porous media studied in this work are characterized by a wide pore size distribution with the relative width $\frac{\Delta R}{R} \sim 1$. Therefore, to describe states of the liquid in such media, variations of the number of neighboring pores in various configurations in the porous medium should be taken into account in the calculations in addition to the theory developed in references [33,34]. This can be done beyond the framework of the mean field approximation used for estimates. As a result, in the case of wide pore size distributions, the energy of the liquid in the disordered porous medium and the volume of the liquid remaining in the porous medium after the removal of excess pressure should be calculated with allowance for a possible breaking of paths for the extrusion of the liquid for two above reasons.

3.2 Energy, volume, and possible states of the nonwetting liquid in the disordered porous medium

Following [33], we consider a spatially disordered porous medium consisting of N pores with various random radii R_i that has the porosity φ and is filled to the degree

of filling θ . Each pore that has the radius R_i and is located at the point \vec{r}_i can be either filled or empty. We introduce the number n_i that is unity and zero if the pore with the radius R_i at the point \vec{r}_i is filled with the liquid and is empty, respectively. The phase space of this system is a $5N$ -dimensional space of the coordinates of the pores, their radii, and filling factors n_i of all N pores. Let $F(\vec{r}_1, R_1, \vec{r}_2, R_2 \dots \vec{r}_N, R_N, n_1, n_2 \dots n_N)$ be the N -particle distribution function of pores in their coordinates \vec{r}_i , radii R_i , and filling factors n_i . The function $F(\vec{r}_1, R_1, \vec{r}_2, R_2 \dots \vec{r}_N, R_N, 0_1, 0_2 \dots 0_N)$ is the N -particle distribution function of empty pores and $F(\vec{r}_1, R_1, \vec{r}_2, R_2 \dots \vec{r}_N, R_N, 1_1, 1_2 \dots 1_N)$ is the distribution function of pores in the completely filled porous medium. At $\theta < 1$, various geometric configurations of filled and empty pores can correspond to the state of the porous medium. Consequently, for the porous medium filled to the degree of filling θ , the multiparticle distribution function of empty and filled pores $F_\theta(\vec{r}_1, R_1, \vec{r}_2, R_2 \dots \vec{r}_N, R_N)$ is degenerate and can be obtained from $F(\vec{r}_1, R_1, \vec{r}_2, R_2 \dots \vec{r}_N, R_N, n_1, n_2 \dots n_N)$ by summing over these configurations, $F_\theta(\vec{r}_1, R_1, \vec{r}_2, R_2 \dots \vec{r}_N, R_N) = \sum_{k=1}^{N_\theta} F(\vec{r}_1, R_1 \dots \vec{r}_N, R_N \{n_i\}_\theta^k)$. The distribution function $F(\vec{r}_1, R_1 \dots \vec{r}_N, R_N \{n_i\}_\theta^k)$ corresponds to $\{n_i\}_\theta^k$ configurations of empty and filled pores such that the total relative volume of filled pores is θ , the index $k = 1 \dots N_\theta$ enumerates these configurations, and N_θ is the maximum number of degenerate configurations. In particular, in the case of non overlapping pores, the multiparticle distribution function of empty and filled pores $F_\theta(\vec{r}_1, R_1, \vec{r}_2, R_2 \dots \vec{r}_N, R_N)$ for the porous medium with the degree of filling θ has the form

$$F_\theta(\vec{r}_1, R_1, \vec{r}_2, R_2 \dots \vec{r}_N, R_N) = \sum_{\{n_i\}} F(\vec{r}_1, R_1, \vec{r}_2, R_2 \dots \vec{r}_N, R_N, \{n_i\}) \times \delta\left(\frac{\sum_{i=1}^N n_i V_i}{\sum_{i=1}^N V_i} - \theta\right),$$

where V_i is the volume of the i th pore.

The total thermodynamic potential, which is the energy of the porous medium filled to the degree of filling θ , can be represented in the form

$$E = \int d\Gamma \sum_{k=1}^{N_\theta} \varepsilon(\vec{r}_1, R_1, \vec{r}_2, R_2 \dots \vec{r}_N, R_N \{n_i\}_\theta^k) \times F_\theta(\vec{r}_1, R_1, \vec{r}_2, R_2 \dots \vec{r}_N, R_N \{n_i\}_\theta^k). \quad (8)$$

We calculate the change δE in the energy of the system at the extrusion of the liquid from a randomly chosen filled pore in the porous medium. Let this pore have the radius R_1 and be located at the point \vec{r}_1 . We assume that the state of the remaining multiparticle system, except for the chosen pore, does not change in this process. In this case, the multiparticle distribution function of empty and filled pores in the porous medium can be represented in

the form

$$F_\theta(\vec{r}_1, R_1, \vec{r}_2, R_2 \dots \vec{r}_N, R_N) = f(\vec{r}_1, R_1) F_\theta(\vec{r}_2, R_2 \dots \vec{r}_N, R_N). \quad (9)$$

Here, $f(\vec{r}_1, R_1)$ is the single-particle distribution function of filled pores normalized to the total number of filled pores in the porous medium filled to the degree of filling θ . In view of equations (8) and (9), the change ΔE in the energy in equation (2) can be represented in the form

$$\delta E = \int \Delta E(\vec{r}_1, R_1) f(\vec{r}_1, R_1) d\vec{r}_1 dR_1. \quad (10)$$

Here, $\Delta E(\vec{r}_1, R_1)$ is the change in the energy of the system at the depletion of one pore

$$\begin{aligned} \Delta E(\vec{r}_1, R_1) &= \int d\vec{r}_2 \dots d\vec{r}_{N-1} dR_2 \dots dR_{N-1} \\ &\quad \times \Delta E(\vec{r}_1, R_1, \vec{r}_2, R_2 \dots \vec{r}_N, R_N) \\ \Delta E(\vec{r}_1, R_1 \dots \vec{r}_N, R_N) &= \sum_{k=1}^{N_\theta} \Delta E(\vec{r}_1, R_1, \vec{r}_2, R_2 \dots \vec{r}_N, \\ &\quad R_N \{\Delta n_1 = 1, n_2 \dots n_{N-1}\}_\theta^k) \\ &\quad \times F_\theta(\vec{r}_2, R_2 \dots \vec{r}_{N-1}, R_{N-1} \{n_2 \dots n_{N-1}\}_\theta^k). \end{aligned} \quad (11)$$

Here, $\Delta E(\vec{r}_1, R_1 \dots \vec{r}_N, R_N)$ is the sum of the energy $\Delta E_s(\vec{r}_1, R_1 \dots \vec{r}_N, R_N)$ of the (porous medium-liquid) interface and the energy $\Delta E_l(\vec{r}_1, R_1 \dots \vec{r}_N, R_N)$ necessary for the formation of menisci in the throats of neighboring pores. It is assumed that the chemical potential of the liquid remains unchanged at its dispersion. This is valid for pores with sizes $R > 1$ nm [41]. With the inclusion of the work pV spent on an increase in the volume of the system V , the expressions for energies $\Delta E_s(\vec{r}_1, R_1 \dots \vec{r}_N, R_N)$ and $\Delta E_l(\vec{r}_1, R_1 \dots \vec{r}_N, R_N)$ can be represented in the form

$$\begin{aligned} \Delta E_s(\vec{r}_1, R_1 \dots \vec{r}_N, R_N) &= pV(\vec{r}_1, R_1) - \delta\sigma(1 - \eta(\vec{r}_1, R_1 \dots \vec{r}_N, R_N))S(\vec{r}_1, R_1), \\ \eta &= \frac{S_m(\vec{r}_1, R_1 \dots \vec{r}_N, R_N)}{S(\vec{r}_1, R_1)}, \\ \Delta E_l(\vec{r}_1, R_1 \dots \vec{r}_N, R_N) &= \sigma\delta S_m(\vec{r}_1, R_1 \dots \vec{r}_N, R_N). \end{aligned} \quad (12)$$

Here, σ is the surface energy of the liquid; $\delta\sigma = (\sigma_{ls} - \sigma_{sg})$ is the difference between the surface energies of the solid-liquid and solid-gas interfaces; $V(\vec{r}_1, R_1)$ and $S(\vec{r}_1, R_1)$ are the volume and surface area of the depleted pore, respectively; $S_m(\vec{r}_1, R_1 \dots \vec{r}_N, R_N)$, $\delta S_m(\vec{r}_1, R_1 \dots \vec{r}_N, R_N)$ are the area of menisci in the pore and the change in the area of menisci at the depletion of the pore, respectively; and p is the pressure of the liquid in the pore. We accept that the area of menisci and the change in the area of menisci at the depletion of the pore are determined only by the nearest environment of the depleted pore. Effects associated with the transfer of the liquid to the pores following the nearest environment of the depleted pore without extrusion from the porous medium are neglected. In this case,

it follows from equations (8)–(12) that $\Delta E(\vec{r}_1, R_1)$ can be represented in the form

$$\begin{aligned} \Delta E(\vec{r}_1, R_1) &= pV(\vec{r}_1, R_1) \\ &\quad - \delta\sigma(1 - \langle\eta(\vec{r}_1, R_1)\rangle) S(\vec{r}_1, R_1) + \Delta E_l, \\ \langle\eta(\vec{r}_1, R_1)\rangle &= \frac{\langle S_m(\vec{r}_1, R_1 \dots \vec{r}_N, R_N) \rangle}{S(\vec{r}_1, R_1)}, \\ \Delta E_l(\vec{r}_1, R_1) &= \sigma \langle \delta S_m(\vec{r}_1, R_1 \dots \vec{r}_N, R_N) \rangle \\ &= \sigma \langle W(\vec{r}_1, R_1 \dots \vec{r}_N, R_N) \rangle \\ &\quad \times S_m(\vec{r}_1, R_1 \dots \vec{r}_N, R_N). \end{aligned} \quad (13)$$

Here,

$$\begin{aligned} \langle S_m(\vec{r}_1, R_1 \dots \vec{r}_N, R_N) \rangle &= \int F_\theta(\vec{r}_1, R_1 \dots \vec{r}_N, R_N) \\ &\quad \times \sum_{k=1}^z s_m(\vec{r}_1, R_1, \vec{r}_k, R_k) d\vec{r}_2, dR_2 \dots d\vec{r}_N, dR_N \\ &= \int d\vec{x} dR_1 S_m(\vec{r}_1, R_1, \vec{x}, R_2) g_2(\vec{r}_1, R_1, \vec{x}, R_2) \end{aligned} \quad (14)$$

and $W(\vec{r}_1, R_1 \dots \vec{r}_N, R_N)$ is the change in the number of menisci at the extrusion of the liquid from the filled pore. In equation (14), $g_2(\vec{r}_1, R_1, \vec{x}, R_2) = g_2(\vec{r}_1, R_1, \vec{r}_1 - \vec{r}_2, R_2)$ is the pair correlation function of pores in the porous medium filled to the degree of filling θ [33]; $s_m(\vec{r}_1, R_1, \vec{x}, R_2)$ is the area of the meniscus of the pores with radii R_1 and R_2 that are located at the points \vec{r}_1 and \vec{r}_2 , respectively; z is the number of pores in the environment of the depleted pore; and integration is performed over the distances $|\vec{x}| < R_1 + R_2$ corresponding to the first coordination sphere. For the spatially isotropic medium, $g_2(\vec{r}_1, R_1, \vec{x}, R_2) = g_2(R_1, |\vec{r}_2 - \vec{r}_1|, R_2)$. The function $g_2(\vec{r}_1, R_1, \vec{x}, R_2)$ for the model of randomly distributed spheres was calculated in references [33,42].

The integration of the pair distribution function over the volume nearest to the depleted pore yields the number $z(R, R_1)$ of the nearest neighbor pores with the radius R_1 for the pore of the radius R :

$$z(R, R_1) = \frac{1}{\varphi V(R_1)} \int_{|R-R_1|}^{|R+R_1|} g_2(R, R_1, \vec{r}) d\vec{r}. \quad (15)$$

Here, $V(R_1)$ is the volume of one pore with the radius R_1 and φ is the porosity. Averaging equation (15) with the normalized pore size distribution function $f(R_1)$, we obtain the average number of the nearest neighbors of the depleted pore with the radius R :

$$z(R) = \int_0^\infty dR_1 f(R_1) z(R, R_1). \quad (16)$$

According to equation (16), the number of nearest neighbors $z(R)$ depends on the radius of the pore R and the width of the distribution $f(R)$. The number of nearest neighbors $z(R)$ as a function of the radius of pores was calculated by equations (15) and (16) for various widths

of the Gaussian distribution $f(R)$. The calculations show that $z(R)$ increases with both the radius of the pore and the width of the pore size distribution $f(R)$. The character of the dependence of $z(R)$ on the radius of the pore R can be understood by considering the pore with the radius R in the disordered porous medium consisting of pores with various radii. In the approximation of constant porosity, with an increase in the radius of the pore R , the number of pores contacting with the given pore increases because of an increase in the area of its surface at a fixed total volume of pores in the local configuration. For this reason, the number of the nearest neighbor pores $z(R)$ with the radius R increases with the radius. The law of this increase was obtained in references [2,43] in the form

$$z(R) \sim R^k, \quad k \sim 3. \quad (17)$$

We calculate the change in the energy of the system at the depletion of one pore. We assume that the liquid flows out of the pore only when at least one of the neighboring pores around the depleted pore belongs to the infinite cluster of filled pores through which the liquid can flow from the granule of the porous medium. In this case, only the states with the infinite cluster of filled pores should be retained in the set of states that is determined by the distribution function $F_\theta(\vec{r}_1, R_1, \vec{r}_2, R_2 \dots \vec{r}_N, R_N)$. It is assumed that the remaining states do not contribute to the change in the number of filled pores. In this case, the quantity W in equation (13) depends on the probability $P(\theta)$ that the pore belongs to the infinite cluster and the number z of the nearest neighbors of the depleted pore with the radius R :

$$W = W(z(R), P(\theta)). \quad (18)$$

The quantity $W = W(z(R), P(\theta))$ is determined as the difference between the average numbers of menisci before and after the depletion of the pore per nearest neighbor. The product of $W = W(z(R), P(\theta))$ by the surface energy of the liquid in the menisci determines the change in the energy of the pore at the extrusion of the liquid from it. The fraction of the trapped liquid in the described experiments was determined after the removal of excess pressure, i.e., at $p = 0$. In this case, according to equations (11)–(13), the change in the energy of the system at the depletion of one pore is given by the expression

$$\begin{aligned} \Delta E(R, \theta_1) &= \Delta E_s(R) + \Delta E_l(R, \theta_1) \\ \Delta E_s(R) &= -\delta\sigma(1 - \eta(R))4\pi R^2, \\ \eta(R) &= \frac{\langle S_m(R, R_1) \rangle}{4\pi R^2}, \\ \Delta E_l(R, \theta_1) &= \sigma \langle W S_m \rangle = 4\pi R^2 \sigma \langle W(z, \theta_1) \rangle \eta(R). \end{aligned} \quad (19)$$

Expressions (19) were obtained under the assumption that the probability W of the change in the number of menisci is independent of their total area: $\langle W S_m \rangle = \langle W \rangle \langle S_m \rangle$. The area of menisci S_m in equations (19) is determined by the nearest environment of the chosen pore. The coefficient $\eta(R)$ is determined by the ratio of the total area of menisci in the pore with the radius R to the area of the

pore in equations (19) can be represented in the form

$$\eta(R) = \frac{1}{4\pi R^2} \int_0^\infty z(R, R_1) s_m(R, R_1) f(R_1) dR_1. \quad (20)$$

Here, $s_m(R, R_1)$ is the area of one meniscus in the throat of the chosen pore with the radius R connected to the pore of the radius R_1 . Thus, to calculate the energy $\Delta E(R, \theta_1)$, it is necessary to calculate the difference between the average numbers of menisci before and after the depletion of the pore per nearest neighbor $\langle W(z, \theta_1) \rangle$ and the connectivity factor $\eta(R)$.

The quantity ΔE_s qualitatively corresponds to the energy of “extrusion” of the nonwetting liquid from the filled pore. The quantity ΔE_l is the change in the total surface energy of menisci in the mouths of all throats connecting the pore with neighboring pores at the extrusion of the liquid from the pore. The difference ΔE_l determines the magnitude and sign of the collective “multiparticle interaction” of the liquid cluster in the pore with its environment and can be both positive and negative.

The dependence of the connectivity factor η for the spherical pore with the radius of R on its radius can be qualitatively estimated from the condition that the average area of pores in the porous medium is constant. The dependence $\eta(R)$ was calculated in references [2,43]. The result has the form:

$$\eta = \left(\frac{R_0}{R} \right)^\alpha. \quad (21)$$

Here, R_0 is the minimum radius of pores in the porous medium and $\alpha \approx 0.3$ [33]. According to equation (20), the connectivity factor of pores η depends on the radius of the pore R and decreases with an increase in the radius of the pore.

The quantity $\langle W(z, \theta_1) \rangle$, which determines the magnitude and sign of the multiparticle interaction, can be calculated by averaging over all possible configurations of filled pores with various radii around the pore with the radius R . We calculate the change in the number of menisci at the extrusion of the liquid from the filled pore W . We consider the configurations of filled pores with close numbers of nearest neighbors z and calculate the difference between the numbers of menisci before and after the depletion of the pore per nearest neighbor $W(z, \theta_1)$. The quantity $\langle W(z, \theta_1) \rangle$ is obtained by averaging over the number of nearest neighbors in the disordered porous medium:

$$W(\theta_1) = \langle W(z, \theta_1) \rangle = \langle W(z, \theta_1) \rangle_z.$$

The number of the nearest neighbors $z(R)$ around the pore with the radius R , which is determined by equation (16), increases with the radius of the pore according to equation (17). Hence, averaging should be performed over the pore size distribution function taking into account the dependence of the number of nearest neighbors on the radius of the pore $z(R)$:

$$W(\theta_1) = \int W(z(R), \theta_1) f(R) dR. \quad (22)$$

To calculate the function $W(z, \theta_1)$, we note that, for the extrusion of the liquid from the pore, this pore should be in contact with the infinite cluster of filled pores through which the liquid can flow. Since such a cluster is formed at $\theta_1 > \theta_c$, $W(z, \theta_1) = 0$ at $\theta_1 < \theta_c$ and the function $W(\theta_1)$ at $\theta_1 > \theta_c$ should be determined as the average difference between the numbers of menisci after and before the depletion of the pore according to the sum

$$\begin{aligned} W(z, \theta_1) &= \sum_{n=0}^{z-1} (1 - \theta_1)^n (P(\theta_1))^{z-n} \frac{z - 2n}{z} \frac{z!}{n!(z-n)!} \\ &= (\theta_1 + P(\theta_1) - 1)(P(\theta_1) - \theta_1 + 1)^{z-1} \\ &\quad + (1 - \theta_1)^z. \end{aligned} \quad (23)$$

Here, $P(\theta_1)$ is the probability that the filled pore belongs to the infinite cluster of filled pores. The first and second factors correspond to the probability that an empty pore is near the infinite cluster of filled pores under the condition that this pore is surrounded by n empty and $z - n$ filled pores and, thereby, contains n menisci. The third factor specifies the difference between the relative numbers of menisci after $(z - n)$ and before (n) the filling of the pore. The combinatory factor takes into account the variants of arrangement of n menisci over the nearest neighbors of the given pore and corresponds to the degeneracy of the local geometric state, i.e., the configurations of this pore and filled pores in the first coordination sphere. Thus, each term in sum (23) describes the change in the number of menisci at a given relation between the numbers of filled and empty pores. Summation in equation (23) includes all possible variants of the mutual location of empty and filled pores and makes it possible to take into account on average variations of the configurations of pores in the space of the disordered porous medium. According to equation (23), the sign of the function $W(z, \theta_1)$ is determined by the competition between terms with the number of empty pores at $n < \frac{z}{2}$ and $n > \frac{z}{2}$ and, therefore, is sensitive to the number of the nearest neighbors $z(R)$. Since $z(R)$ depends both on the radius of the pores and on the width of the pore size distribution $f(R)$ according to equations (16) and (17), the magnitude and sign of the function $W(\theta_1)$ can also depend significantly on the width of the pore size distribution at least for degrees of filling near the percolation threshold $\theta \geq \theta_c$.

Figure 5 shows the dependence $W(\theta_1)$ calculated by equations (22) and (23) for various distribution functions $f(R)$. These dependences present the change in the energy of the multiparticle interaction of the liquid cluster in the filled pore at various configurations of its environment under variation of the degree of filling. The calculations were performed with the dependence $P(\theta_1)$ taken from [44].

At $\theta_1 \rightarrow 1$, W is positive and approaches 1, corresponding to the change in the number of menisci at the extrusion of the liquid from one pore in the completely filled porous medium. The sign of $W(\theta_1)$ corresponds to the effective collective attraction of the liquid cluster in the pore to its environment. A decrease in the degree of filling results in a decrease in $W(\theta_1)$ because of a decrease

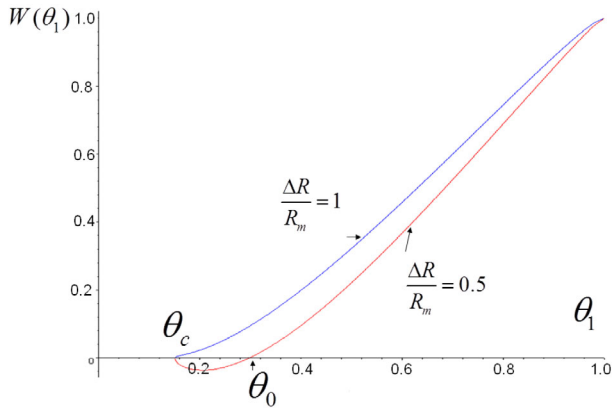
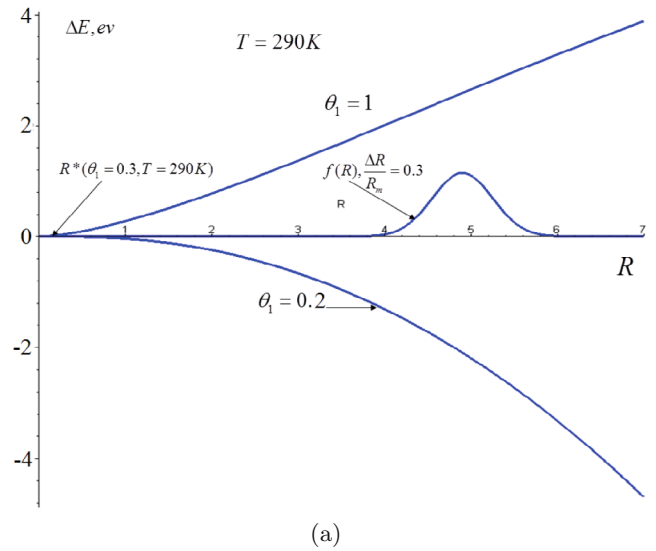


Fig. 5. Quantity $W(\theta_1)$ versus the degree of filling at the porosity $\varphi = 0.45$ and various half-widths of the Gaussian distribution function $f(R) \sim \exp(-\frac{(R-R_m)^2}{(\Delta R)^2})$, $R_m = 4$.

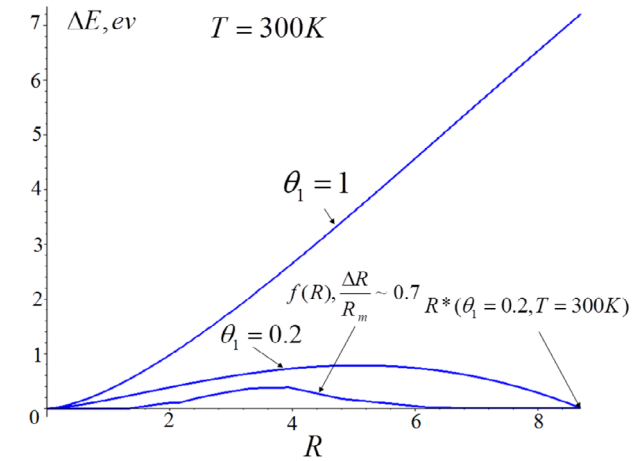
in the number of neighboring filled pores and an increase in the number of menisci around the filled pore at the extrusion of the liquid. A further decrease in the degree of filling is accompanied by a decrease in the number of menisci after the extrusion of the liquid from the pore and by the change of the sign of $W(\theta_1)$ at $\theta_1 = \theta_0$ (see Eq. (23)), which corresponds to the change of the effective collective “multiparticle” attraction to the effective repulsion. When the degree of filling is below the percolation threshold, $\theta_1 < \theta_c$, the infinite cluster is absent. In this case, $W(\theta_1 \leq \theta_c) = 0$ and, according to equations (1) and (19), extrusion is possible only from individual clusters connected with the boundary of the porous medium.

As can be seen in Figure 5, an increase in the width of the pore size distribution results in an increase in the effective multiparticle attraction of liquid nanoclusters in pores, and a decrease in the width of the pore size distribution can be accompanied by the change of the sign of $W(\theta_1)$ at $\theta_1 = \theta_0$. Since the number of the nearest neighbors $z(R)$ increases with the width of the pore size distribution, according to equation (23), an increase in the width of the distribution $\Delta R/R$ leads to an increase in the number of the nearest neighbors and to the resulting increase in $W(\theta_1)$ because of the power-law dependence of $W(z, \theta_1)$ on z (see Eq. (23)). For narrow pore size distributions, the effective multiparticle attraction of the liquid cluster in the filled pore to neighboring clusters changes at a certain degree of filling to their effective repulsion. Together with the repulsion of the nonwetting liquid from walls, this can result in the negativeness of the potential barrier $\delta A(p=0)$ in equation (1), and the liquid flows out of the pore.

Expressions (18) and (23) allow the calculation of the change in the energy of the system consisting of the nonwetting liquid and disordered nanoporous medium at the extrusion of the liquid from an arbitrary pore. This makes it possible to qualitatively analyze the interval of pores in which the liquid can remain for the extrusion expectation time in the performed experiments at various temperatures and various degrees of preliminary filling with the



(a)



(b)

Fig. 6. Change in the energy of the liquid in the pore $\Delta E(R)$ for $\frac{\sigma}{\delta\sigma} = 4$ at the degrees of filling $\theta_1 = 1$ and $\theta_1 = 0.2$ versus the radius of the pore for (a) the narrow pore size distribution with the relative width $\frac{\Delta R}{R_m} \sim 0.3$ and (b) the wide pore size distribution with the relative width $\frac{\Delta R}{R_m} \sim 0.7$.

use of the probability of extrusion (1). Figures 6 and 7 show the calculated dependences of the change in the surface energy ΔE at the degrees of filling $\theta_1 = 0.2, 1.0$ and the temperatures $T = 290, 300$ K and $\theta_1 = 1.0$ at the temperatures $T = 290, 320$ K, respectively. In these calculations, the pore size distribution was taken in the Gaussian form with relative widths $\frac{\Delta R}{R} = 0.3, 0.7$ and $\frac{\sigma}{\delta\sigma}$ was taken to be 4.

According to Figure 6a, the activation barrier ΔE for the decay of the metastable state of local configurations can change sign at an increase in the degree of filling from 0.2 to 1 so that complete extrusion at $\theta_1 = 0.2$ can change to the complete entrapment of the liquid for pores with any sizes in the distribution $f(R)$. An increase in the temperature by 10 K and an increase in the relative width of

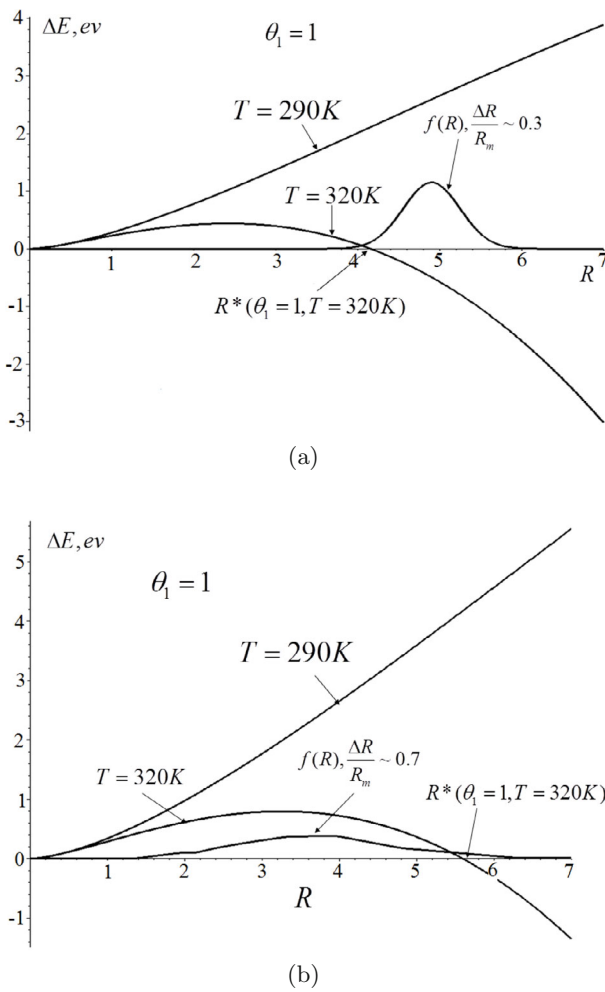


Fig. 7. Change in the energy of the liquid in the pore $\Delta E(R)$ for $\frac{\sigma}{\delta\sigma} = 4$ at the degree of filling $\theta_1 = 1$ for temperatures $T = 290$ and 320 K versus the radius of the pore for (a) the narrow pore size distribution with the relative width $\frac{\Delta R}{R_m} \sim 0.3$ and (b) the wide pore size distribution with the relative width $\frac{\Delta R}{R_m} \sim 0.7$.

the distribution to $\frac{\Delta R}{R_m} \sim 0.7$ can result in the complete entrapment of the liquid not only at $\theta_1 = 1$, but even at $\theta_1 = 0.2$ (see Fig. 6a).

Figure 7 shows possible scenarios of the formation of the state of the dispersed liquid when the liquid after preliminary complete filling can be trapped in pores with a certain size if the activation barrier ΔE changes sign and becomes negative at $R = R^*(\theta_1, T)$, $R_0 < R^* < R_{\max}$ (R_0 , R_{\max} are the minimum and maximum sizes of pores in the medium, respectively). According to equations (19) and (21), it follows from the condition $\Delta E = 0$ that

$$R^*(\theta_1, T) = R_0 \left(1 + \frac{\sigma_{lg}}{\delta\sigma} W_1(\theta_1) \right)^{\frac{1}{\alpha}}. \quad (24)$$

In the case of a narrow distribution with the relative width $\frac{\Delta R}{R_m} \sim 0.3$, the liquid at $T = 320$ K and $\theta_1 = 1$ cannot flow out of pores with the radius $R_0 < R < R^*(\theta_1, T)$, whereas entrapment at $T = 290$ K and $\theta_1 = 1$ is possible

in all pores (see Fig. 7a). For a wider distribution with the relative width $\frac{\Delta R}{R_m} \sim 0.7$, entrapment at $\theta_1 = 1$ and $T = 320$ K is possible in pores with the radius $R < R^*(\theta_1, T)$ (see Fig. 7b).

We calculate the volume fraction of the liquid in the metastable state. Let pore size distribution functions be normalized to the degree of filling of pores in the porous medium θ_1 . Then, the volume fraction of the liquid in the metastable state in the porous medium θ_m filled to the degree of filling θ_1 is determined by the integral of the product of the pore distribution function by the volume of pores in the range from the minimum radius of pores R_0 in the porous medium to the critical radius $R^*(\theta_1, T)$:

$$\theta_m = \frac{\theta_1 \int_{R_0}^{R^*(\theta_1, T)} R^3 f(R) dR}{\int_{R_0}^{\infty} R^3 f(R) dR}. \quad (25)$$

Expression (25) gives the volume fraction of the liquid in the porous medium that is in the pores for which the potential barrier average over configurations that separates the empty porous medium and dispersed liquid is finite at the extrusion of the liquid from a pore belonging to the percolation cluster of connected pores with various sizes filled with the liquid. It follows from equation (24) that the critical radius $R^*(\theta_1, T)$ separating pores in the metastable state and empty pores in the porous medium becomes equal to the minimum radius of pores in the porous medium at a certain degree of filling. This condition corresponds to the disappearance of the metastable state of the liquid in the porous medium. According to equation (24) and Figure 5, an increase in the width of the distribution results in an increase in the effective attraction between interacting clusters (see Fig. 5) and, consequently, in an increase in the critical radius $R^*(\theta_1, T)$. With an increase in $\frac{\Delta R}{R_m}$ and, as a result, with an increase in $W(\theta_1)$, the potential barrier separating the metastable state and the state of the porous medium without the liquid increases simultaneously with $R^*(\theta_1, T)$ (see Fig. 7). It can also be seen in Figure 6 that the possibility of the disappearance of the metastable state of the liquid in the porous medium depends on the width of the pore size distribution.

The total volume fraction $\theta_2(\theta_1)$ of the liquid remaining in the porous medium filled to the degree of filling θ_1 for a macroscopically long time is determined by the sum of the terms corresponding to the volume fraction of the liquid $\theta_m(\theta_1)$ in configurations corresponding to the metastable state of the liquid in pores and the volume fractions of the liquid in pores disconnected from the infinite cluster $\theta_s(\theta_1)$ for which paths for extrusion are absent (see Fig. 4):

$$\theta_2(\theta_1) = \theta_m(\theta_1) + \theta_s(\theta_1). \quad (26)$$

This volume fraction is due to the geometry of the space of pores and is associated with those filled pores that appear because of the decomposition of the infinite cluster of filled pores.

The volume fraction θ_s of the liquid owing to the geometry of the space of pores is determined by the fraction of pores that are in clusters in which the liquid is trapped because of the absence of possible paths for extrusion. It is independent of the temperature and energy of the interfaces and is determined by the product of the probability that these pores do not belong to the infinite cluster of filled pores under the condition that the surrounding pores are empty and includes all possible configurations of the mutual arrangement of filled and empty neighboring pores. In reference [2], it was shown that $\theta_s(\theta_1)$ is determined by the integral of the difference between the total degree of filling θ_1 and the relative number of filled pores belonging to the infinite cluster $P(\theta_1)$. Calculations show that the quantity $\theta_s(\theta_1)$ for known dependences $P(\theta_1)$ [45] rapidly approaches a constant value and can be treated as constant already at $\theta_1 \sim (1.1 \div 1.2)\theta_c$.

According to the above consideration and equations (18) and (25), the following states of the nonwetting liquid in the disordered nanoporous medium are possible.

1. The quantity ΔE_s corresponding to the energy of the “extrusion” of the nonwetting liquid from the filled pore is larger than ΔE_l determining the change in the total surface energy of menisci in the mouths of all throats connecting the pore with neighboring pores at the extrusion of the liquid from the pore for a given temperature range and for all degrees of filling θ_1 (line for $\theta_1 = 0.2$ in Fig. 6a). In this case, the nonwetting liquid cannot be in the metastable state in the porous medium and the volume fraction $\theta_2(\theta_1)$ of the liquid remaining in the porous medium filled to the degree of filling θ_1 is determined by the volume fraction $\theta_s(\theta_1)$ of the liquid remaining in pores disconnected from the infinite cluster. In the absence of evaporation, the barrier for the extrusion of the liquid from these pores is infinite. For this reason, the volume fraction of the liquid $\theta_s(\theta_1)$ is independent of the temperature and the decay time of this state is infinitely large. This state can exist in systems for which $W_1(\theta_1)$ has any sign, including systems for which $W_1(\theta_1)$ is sign alternating, e.g., for systems with a narrow pore size distribution.
2. The quantity ΔE_s is smaller than the quantity ΔE_l for a given temperature range and any degree of filling θ_1 (see Figs. 6b and 7b). In this state, the nonwetting liquid in the porous medium in the given temperature range is in a metastable state at any degree of filling. The volume fraction $\theta_2(\theta_1)$ of the liquid remaining in the porous medium is determined by the sum of the terms corresponding to the volume fraction $\theta_m(\theta_1)$ of the liquid in the configurations corresponding to the metastable state of the liquid in pores and the volume fractions $\theta_s(\theta_1)$ of the liquid in pores that are disconnected from the infinite cluster and for which paths for extrusion are absent. The volume fraction $\theta_2(\theta_1)$ of the liquid for this state is $\theta_2(\theta_1) \sim \theta_1$ (see Figs. 6b and 7b) and depends slightly on the temperature in a given temperature range. The decay time of this state decreases with an increase in the temperature. This state can exist in systems for which $W_1(\theta_1) > 0$, i.e.,

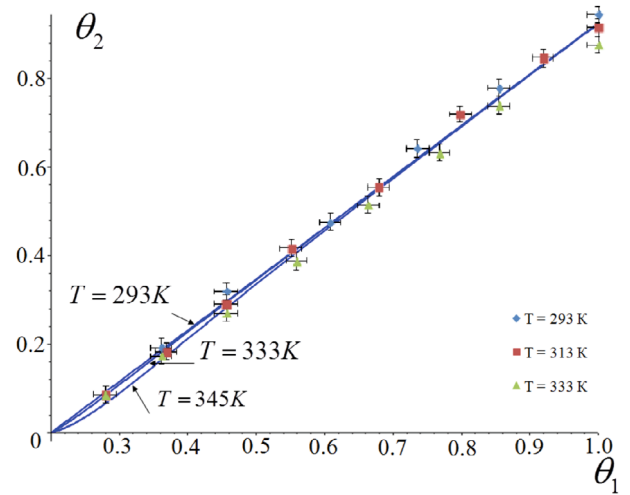


Fig. 8. Fraction of the nonwetting liquid (water) trapped in the porous medium Fluka 100 C8-water versus the degree of filling at the temperatures $T = 293, 333,$ and 345 K (solid lines). Points – experimental data.

for systems with a broad pore size distribution (see Figs. 6b and 7b).

3. In the given temperature range and in the interval $0 < \theta_1 < \theta_c$ of the degree of filling, the quantity ΔE_s is larger than the quantity ΔE_l , whereas the quantity ΔE_s in the range $\theta_c < \theta_1 < 1$ is smaller than ΔE_l (see Figs. 6a and 7a). Systems in this state will undergo a dispersion transition at $\theta_1 = \theta_c$. The volume fraction $\theta_2(\theta_1)$ of the liquid remaining in the porous medium is determined at $0 < \theta_1 < \theta_c$ by the volume fraction $\theta_s(\theta_1)$ of the liquid in pores disconnected from the infinite cluster for which paths for extrusion are absent. At $\theta_c < \theta_1 < 1$, the volume fraction is determined by the sum of the terms corresponding to the volume fraction $\theta_m(\theta_1)$ of the liquid in configurations corresponding to the metastable state of the liquid in pores and the volume fraction $\theta_s(\theta_1)$ of the liquid in pores disconnected from the infinite cluster for which paths for extrusion are absent. The volume fraction $\theta_2(\theta_1)$ of the liquid and the decay time of such a state depend on the temperature. This state can exist in systems for which $W_1(\theta_1)$ has any sign.

Calculations with equations (18), (25), and (26) were performed for the qualitative description of the experimental data obtained. According to equation (1), the liquid in the experiment time cannot flow out of pores with the radius determined by the condition $\Delta E > T$. In the presented qualitative description, it was assumed that the liquid in the experiment time is trapped in all pores with the radii $R < R^*$ determined by the condition $\Delta E = 0$ and equation (24).

Figures 8–10 show the dependences of the fraction of the nonwetting liquid remaining in the porous body on the degree of filling at various temperatures calculated by equations (18), (25), and (26) with the parameters (φ, \bar{R}) of the porous medium and liquid equal to the values

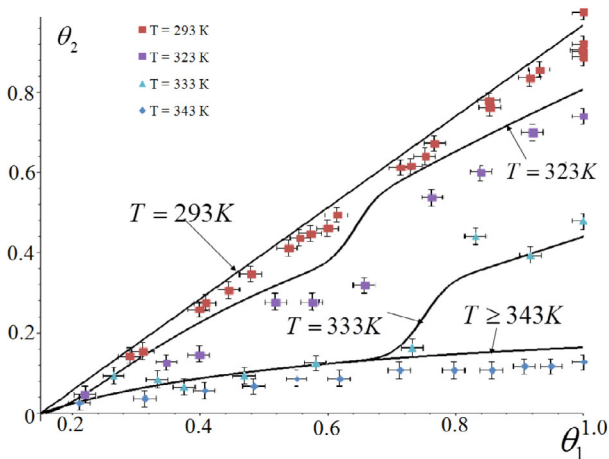


Fig. 9. Fraction of the trapped nonwetting liquid for the Fluka 100 C18-water system versus the degree of filling at the temperatures $T = 293$, 323 , and 333 K and $T \geq 343$ K (solid lines). Points – experimental data.

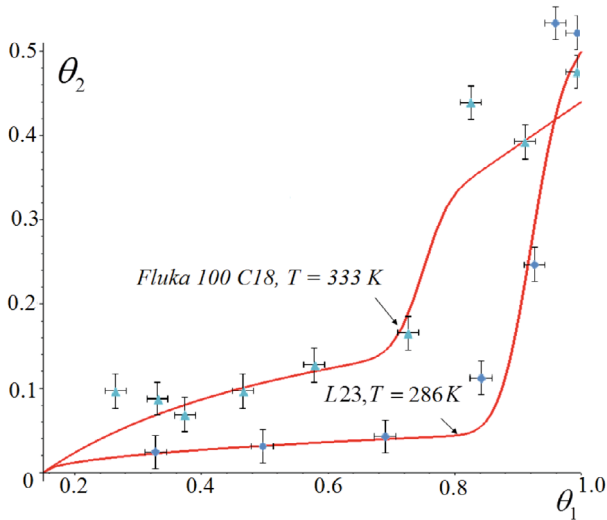


Fig. 10. Fraction of the trapped nonwetting liquid for the L23-water and Fluka 100 C18-water systems versus the degree of filling at temperatures $T = 286$ and 333 K, respectively (solid lines). Points – experimental data.

obtained in independent experiments (see Sect. 2). The surface tension coefficient of water and its temperature dependence were taken from [40,46]. The surface tension coefficient of water at $T = 293$ K is 72.9 mJ/m^2 [40,46]. The quantity $\delta\sigma$ and its temperature dependence were determined in terms of the filling pressure by the method described in reference [32] for the L23-water system. The filling pressure for the Fluka 100 C18-water and Fluka 100 C8-water systems was 150 and 130 atm, respectively. The $\delta\sigma$ value estimated from these data at $T = 293$ K was 20 and 17 mJ/m^2 for the Fluka 100 C18-water and Fluka 100 C8-water systems, respectively. The distribution functions (Fig. 1) obtained from analysis of the adsorption dependences for nitrogen were used in the calculations.

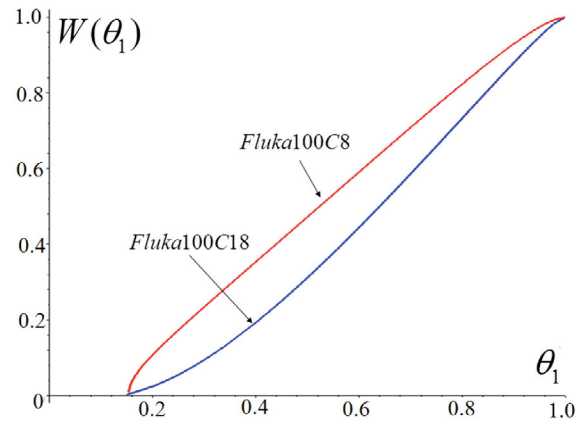


Fig. 11. Dependences $W_1(\theta_1)$ for Fluka 100 C8 and Fluka 100 C18.

According to Figures 8 and 9, several states of the systems under consideration can exist:

- the filled volume fraction θ_2 for the Fluka 100 C8-water system increases almost linearly with the degree of filling θ_1 in the entire time range 293–345 K;
- a linear dependence of the volume fraction of the trapped liquid on the degree of filling is observed for the Fluka 100 C18-water system at a temperature of 293 K. In the temperature range of 323–333 K, a dispersion transition is observed: the liquid flows out of pores when the degree of filling is less than $\theta_{c1} \sim 0.6$. At a temperature of 343 K, the dispersion transition disappears and the volume fraction of the trapped liquid depends slightly on the degree of filling at $T \geq 343$ K.

Figure 10 shows the calculated qualitative dependences of the fraction of the trapped nonwetting liquid for the L23-water and Fluka 100 C18-water systems at temperatures $T = 286$ and 333 K, respectively. It can be seen that the dispersion transition in the Fluka 100 C18-water system occurs at higher temperatures as compared to the L23-water system. Figure 10 indicates that the calculated dependences qualitatively describe the experimental data (Fig. 3).

We now analyze the reasons for the appearance of various states of the systems under study. The dependences $W_1(\theta_1)$ for Fluka 100 C8 and Fluka 100 C18 are shown in Figure 11, where it can be seen that $W_1(\theta_1) > 0$ for these systems and $W_1(\theta_1)$ for the Fluka 100 C8-water system is larger than that for the Fluka 100 C18-water system. The ratio $\frac{\sigma}{\delta\sigma}$ for the Fluka 100 C8-water system is 4.5 at a temperature of $T = 293$ K and decreases to 3 at $T = 345$ K. The average connectivity factor of pores for this system at a porosity of $\varphi = 0.49$ is $\eta \sim z \left(\frac{R_0}{R} \right)^2 \sim 0.8$. The ratio of the change ΔE_l in the energy of the liquid in the mouths of the throats connecting the pore with neighboring pores at extrusion in the temperature range under consideration to the change ΔE_s in the energy of the boundary wall of the frame in the pore is $\Delta E_l / \Delta E_s \sim \eta \sigma W_1(\theta_1) / (\delta\sigma(1-\eta)) \sim 20W_1(\theta_1)$. It can be seen in Figure 11 that $20W_1(\theta_1) > 1$ for these systems

throughout the entire range of the degree of filling above the percolation threshold θ_c . Therefore, the change ΔE_l in the energy of the liquid in the mouths of throats at extrusion for the Fluka 100 C8-water system at temperatures 293–343 K is larger than the change ΔE_s in the energy of the boundary wall of the frame in the pore at any degree of filling except for the range near the percolation threshold θ_c . The system of clusters is in a “condensed” state, where the critical radius $R^*(\theta_1, T)$ separating empty pores and pores in the metastable state is much larger than the minimum radius R_0 because $W(\theta_1) \leq 1$ for $\frac{\sigma}{\delta\sigma} \sim 4$ (see Fig. 11) and estimates give

$$\begin{aligned} R^*(\theta_1, T) &= R_0 \left(1 + \frac{\sigma_g}{\delta\sigma} W_1(\theta_1)\right)^{\frac{1}{\alpha}} \\ &\sim R_0 \left(\frac{\sigma_g}{\delta\sigma} W_1(\theta_1)\right)^{\frac{1}{\alpha}} \gg R_0. \end{aligned}$$

Consequently, the integral

$$\int_{R_0}^{R^*(\theta_1, T) \gg R_0} R^3 f(R) dR \approx \int_{R_0}^{\infty} R^3 f(R) dR$$

for this state of the Fluka 100 C18-water system is independent of the degree of filling, and the volume fraction of the liquid remaining in the porous medium increases linearly with the degree of filling

$$\theta_m = \frac{\int_{R_0}^{R^*(\theta_1, T) \gg R_0} R^3 f(R) dR}{\int_{R_0}^{\infty} R^3 f(R) dR} \sim \theta_1$$

(see Fig. 10).

We now consider the state of the Fluka 100 C18-water system. For this system, the ratio $\frac{\sigma}{\delta\sigma}$ is 3.5 at a temperature of $T = 293$ K, decreases to about 1 at $T = 343$ K, and is smaller than unity at temperatures above $T_c = 343$ K. The average connectivity factor of pores for this system at a porosity of $\varphi = 0.4$ is $\eta \sim z\left(\frac{R_0}{\langle R \rangle}\right)^2 \sim 0.6$ ($R_0 \sim 1.5$ nm, $\langle R \rangle \sim 4$ nm, $z \sim 4$). For this reason, the ratio of the change $\Delta E_l \sim \eta\sigma W_1(\theta_1)$ in the energy of the liquid in the mouths of throats at extrusion in the temperature range of 293–343 K to the change $\Delta E_s \sim \delta\sigma(1 - \eta)$ in the energy of the boundary wall in the pore varies from $\sim 5W_1(\theta_1)$ at $T = 293$ K to $\sim W_1(\theta_1)$ at $T = 343$ K. At low temperatures $T < T_{c1}$, where $T_{c1} \sim 330$ K, ΔE_l is larger than ΔE_s at any degree of filling except for the range near the percolation threshold θ_c . Therefore, the system of liquid clusters in pores at $T < T_{c1}$ is in the “condensed” state, where the critical radius $R^*(\theta_1, T)$ separating empty pores and pores in the metastable state is much larger than the minimum radius R_0 . For this reason, the volume fraction of the liquid remaining in the porous medium for this state increases linearly with the degree of filling $\theta_m \sim \theta_1$. In the temperature range $T_c > T > T_{c1}$, the behavior of the system is determined by the competition between comparable energies ΔE_s and ΔE_l . In this

case, a dispersion transition occurs at the degree of filling θ_{c1} for which the change ΔE_s in the energy of the boundary wall in the pore becomes equal to the change ΔE_l in the energy of the liquid in the mouths of throats at extrusion (see Figs. 9 and 10). According to Figures 9 and 10, $\theta_{c1} \sim 0.6$, which does not contradict experimental data. At temperatures above $T_c = 343$ K, the ratio $\frac{\sigma}{\delta\sigma}$ for the Fluka 100 C18-water system is smaller than unity. In this case, the change ΔE_s in the energy of the boundary wall in the pore becomes equal to the change ΔE_l of the energy of the liquid in the mouths of throats at extrusion. The critical radius $R^*(\theta_1, T)$ becomes about the minimum radius R_0 and $\theta_m(\theta_1)$ vanishes (see Eq. (24)). Hence, the volume fraction $\theta_2(\theta_1)$ of the liquid remaining in the porous medium at $T > T_c = 343$ K is determined by the volume fraction θ_s of the liquid caused by the geometry of the space of pores and is independent of the temperature (see Fig. 11). The appearance of various states in systems under study is due to competition between the change ΔE_s in the energy of the boundary wall in the pore and the change ΔE_l in the energy of the liquid in the mouths of throats at extrusion, which correspond to the effective multiparticle interaction and are given by equations (19).

4 Conclusions

To summarize, three different states of a dispersed non-wetting liquid (water) in the Fluka 100 C8 and Fluka 100 C18 disordered porous media, as well as transitions between these states under variation of the temperature and the degree of filling, have been qualitatively described in this work. It has been shown that the appearance of such states is determined by the width of the pore size distribution function $f(R)$. Since dependences $f(R)$ obtained from nitrogen desorption isotherms provide only qualitative representation of these distributions, a qualitative description of the revealed states and transitions between them has been given. The appearance of these states and transitions is due to the competition between the effective repulsion of the nonwetting liquid from the wall of a pore, which is responsible for the “extrusion” of the liquid from the pore, and the effective collective multiparticle attraction of the liquid cluster in the pore to clusters in the neighboring connected pores. This collective multiparticle attraction appears because the surface energy of the system of liquid clusters in completely filled pores is not the sum of the surface energies of all independent liquid clusters. Clusters can be in contact with each other in neighboring pores connected through throats. A liquid-gas interface is absent in the mouths of these throats if the pore is connected through throats with neighboring filled pores. This means that the surface energy of two clusters in the neighboring pores is lower than the surface energy of two independent clusters by the energy of the liquid-gas interface in the mouth of the throat connecting these filled pores. A decrease in the surface energy can be considered as the negative energy of the interaction between two liquid clusters, i.e., as the effective attraction

between interacting clusters. The interaction between liquid clusters can be responsible for the situation where the total energy of “the multiparticle attractive interaction” becomes higher than the energy of the liquid-solid interface. In this case, the system of clusters becomes “condensed”. In this state, the entrapment of the liquid in the porous medium is energetically favorable; i.e., extrusion is energetically unfavorable.

The magnitude of the effective “multiparticle attraction” of the liquid cluster in the disordered nanoporous medium is determined by the energies of interfaces and depends on the temperature because of the temperature dependence of the surface tension coefficients σ_{lg} , σ_{ls} , σ_{sg} at the phase interfaces. The sign of the effective “multiparticle attraction” of the liquid cluster in the disordered nanoporous medium is determined by the spatially inhomogeneous geometric configurations of the liquid cluster in the pore and its environment. It depends on the degree of filling of the porous medium and is determined by the pore size distribution function $f(R)$, variation of the number of neighbors in the system of pores, and variation of the local configuration of the pore and its environment consisting of filled and empty pores on the rough shell of the percolation cluster. Depending on the width of this distribution, various local configurations are possible in the porous medium; e.g., a pore can be surrounded by smaller pores or by a smaller number of neighboring pores. For this reason, various configurations of empty and filled pores are formed in the porous medium and, as a result, the “multiparticle interaction” between liquid clusters appears with various magnitudes and signs. Variations of local configurations of the pore and its environment at the extrusion of the liquid from the pore can result in the breaking of the infinite cluster of filled pores and in the formation of clusters containing of a finite number of filled pores for which paths for extrusion are absent. In this state, the liquid remains in the porous medium because paths for its extrusion are absent.

The energy of “interaction” in the disordered porous medium fluctuates because of various spatially inhomogeneous geometric configurations of the liquid cluster in the pore and its environment, leading to the formation of a random potential relief for the extrusion of the liquid from different pores. The magnitudes of peaks and dips in this potential relief determine the set of the configurations of empty and filled pores from which the liquid flows. If the number of such configurations is macroscopically large, they form various metastable states of the nonwetting liquid in the form of an ensemble of liquid nanoclusters in pores. The potential barrier between metastable states has been calculated in this work in the mean field approximation.

In the described picture, the first of the revealed states appears if the “effective multiparticle repulsion” between liquid clusters is smaller than their effective multiparticle “attraction” for a given temperature range and any degree of filling. In this case, the nonwetting liquid in the porous medium is in a metastable state in a given temperature range at any degree of filling. The volume frac-

tion of the liquid in this state increases linearly with the degree of filling and depends slightly on the temperature. The potential barrier for the extrusion of the liquid in this metastable or quasi-nonergodic [28] state is finite. The decay time of such a state decreases with an increase in the temperature.

The second of the revealed states appears if the “effective repulsion” in a certain range of the temperature and the degree of filling is stronger than the effective “attraction”, whereas the “effective repulsion” beyond this range is weaker than the effective “attraction”. Systems in this state will undergo a dispersion transition at the critical degree of filling and the critical temperature, which are determined from the condition of the equality of the effective “attraction” and “effective repulsion”. The barrier for the extrusion of the liquid in this state is finite. This state is also metastable or quasi-nonergodic. The volume fraction of the liquid, as well as the decay time of such a metastable state, is finite and depends on the temperature.

The third state of the liquid remaining in the porous medium is determined by the volume fraction of the liquid trapped in pores that are formed because of the breaking of the infinite cluster of filled pores and are disconnected from the infinite cluster. The barrier for the extrusion of the liquid from these pores is infinite. This state is nonergodic [47]. The volume fraction of the liquid in this state is independent on the temperature and the decay time of such a state is infinitely long.

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