Hysteresis of Percolation Transition and Relaxation of Fast and Slow States of the System Nanoporous Medium - Non-Wetting Liquid

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Abstract. In the present paper we present the results of experimental and theoretical studies of intrusion-extrusion and relaxation of non-wetting liquid in three Fluka porous media. New data on hysteresis of intrusion-extrusion and dependence of the degree of filling of a porous body on time in the process of extrusion were obtained experimentally. It has been established that in all the conducted experiments the liquid extrusion took place in two stages: at the first stage of fast relaxation the characteristic time of outflow is several seconds, at the second stage of slow relaxation the characteristic time is several hundred seconds. The experimental data obtained are described in the theoretical model [1]. For the studied porous media, the existence at the initial moment of time of local states with short leakage times (a few seconds or less) and states with large leakage times (hundreds of seconds) was established. Porous bodies in which the coexistence of fast and slow states at the initial moment of time is established are investigated for the first time.

1. Introduction
Research of nanoporous mediums–non-wetting liquid systems is one of the urgent tasks of fundamental and applied research [1-10]. Interest in such research is connected with a number of unusual effects typical of such systems. Such effects include, first of all, the observed hysterisis of filling-flow of non-wetting liquid, which leads to the absorption of mechanical energy in the intrusion-extrusion cycle [5,8,11-15]. Other characteristic features of these systems include anomalously slow relaxation of the non-wetting liquid in a porous medium [1], possible non-outflow of the liquid and transition to dispersion [16-19], strong dependence of relaxation kinetics on temperature [1,20,21], etc. So far, porous media with different pore shape, porosity, specific surface, specific volume, mean radius and pore size distribution have been studied [2,7,8,11-15]. Basically in these works equilibrium properties were studied - experiments were carried out at low speed of compression of the system, when the pressure growth rate in the system liquid-porous medium was \((10^{-3} \text{–} 1)\) atmospheres.

From a theoretical point of view, there is still no consensus on the physical mechanisms that lead to the detected phenomena. The existing theoretical models are not able to describe...
the discovered effects and to reveal the physical mechanisms from the origin of a common position.

In this paper we present the results of experimental and theoretical studies of intrusion and extrusion of non-wetting liquid in three porous Fluka media differing in porosity and chemical modifications. As measurements have shown, these porous media are characterized by a relatively small value of the average pore radius ($\bar{R} \sim 3.7 \div 3.8$ nm) and a wide distribution of pores in size ($\Delta R / \bar{R} \sim 0.4$), which differs significantly from the previously studied porous medium Libersorb23 [1]. We experimentally obtained new data on the dependence of the pressure on the degree of filling of the porous body in the processes of intrusion and extrusion and the dependence of the degree of filling on time in the process of extrusion. It was found out that in all the experiments the fluid outflow took place in two stages: at the first stage of fast relaxation the characteristic time of outflow is several seconds, at the second stage of slow relaxation the characteristic time of several hundred seconds. In the framework of the theoretical model [1], this can be interpreted as the existence at the initial moment of time of local states with short outflow times (a few seconds or less) and states with large outflow times (hundreds of seconds). Porous bodies in which the coexistence of fast and slow states at the initial moment of time is established have been studied for the first time.

2. Experimental section

2.1. Experimental setup

![Figure 1](image.png)

Figure 1. Scheme of the high pressure chamber

In the present work the measurements were carried out with a high pressure chamber, the scheme of which is presented in Fig. 1. The chamber is assembled and consists of body 1, bushing 2, rubber ring seal 3, cover 4, stem 5, seals 6. Inside the chamber there is a porous body 7 in the liquid-permeable 8 container 9. Body 1, plug 2 and cover 4 are made of titanium alloy. Measurement of pressure in the chamber and changes in the internal volume of the chamber was carried out on an experimental stand, the scheme of which is shown in Fig. 1. Two metal plates
Figure 2. Scheme of the experimental stand.

1 and 2 are rigidly connected with each other by means of bearing rods 3. The rods are also guides for mobile platform 4, which can be moved between plates 1 and 2. Additional rigidity of the stand in the horizontal plane is provided by moving platform 4 between two guiding rods 5. Moving the platform in the vertical direction is carried out with the help of the jack 6 mounted on the bottom plate 1. The high pressure chamber is mounted on the load cell 7, located on the platform 4 in such a way that the chamber stem rests on the upper plate 2. The movement of the platform upwards causes the stem to enter the chamber and increase the pressure in it. At the same time, the sensor 7 records the force of \( F \), with which the weight acts on the stems associated with the pressure in the chamber with a ratio of \( p = F/S \), where \( S \) — the area of the stem. When the platform moves downwards, the rod leaves the chamber and the pressure in it drops. Measuring of platform movement and rod insertion depth into the chamber is carried out with the help of a rheochord slide type movement sensor. Sensor 8 is fixed on rod 3, and the slider movement is carried out with the help of the associated rod, the free end of which is fixed on the platform 4. Readings of the force sensor 7 and movements 8 through the amplifier are received by the ADC and recorded by the computer.

| Porous medium                      | \( V_s \) m\(^3\)/g | \( S_s \) m\(^2\)/g | \( \langle r \rangle \), nm |
|------------------------------------|----------------------|----------------------|-----------------------------|
| Fluka 100C8 C1 (60755–50 G)        | 0.54                 | 263                  | 3.8                         |
| Fluka 100C18 C1 (60758–50 G)       | 0.41                 | 179                  | 3.8                         |
| Fluka 100C18 (60756–50 G)          | 0.37                 | 147                  | 3.7                         |

Table 1. Characteristics of the studied porous media, measured by the method of low-temperature sorption of nitrogen. \( V_s \) — specific pore volume, \( S_s \) — specific pore surface area, \( \langle r \rangle \) — average pore radius.

With the help of the described equipment the industrial samples of porous media Fluka 100C8 C1 (60755–50 G) and Fluka 100C18 C1 (60758–50 G) with additional chemical modification made at the Faculty of Chemistry of Lomonosov Moscow State University, as well as the industrial sample Fluka 100 C18 (60756-50 G) without chemical modification were studied. Characteristics of porous media were determined by the method of low-temperature sorption of nitrogen and are presented in the table 1. Distilled water was used as a liquid. Measurements were carried out as follows. The sample was placed in a high pressure stainless steel chamber. The free volume was filled with liquid. A bushing with a rod bore was then inserted and secured with a cover. The
change in the internal volume of the chamber was achieved by moving the 10 mm diameter rod inside the chamber. The rod was moved by a jack. The force acting on the rod was recorded by a force sensor. The change in the internal volume of the chamber was determined by the depth of penetration of the stem into the chamber with the help of a reversible slide type movement sensor. Computer readings of the sensors were recorded via ADC [22].

2.2. Experimental results

![Figure 3. Dependence of liquid pressure $p$ (without taking into account atmospheric pressure) on a degree of filling volume of pores in cycles of intrusion-extrusion for porous medium Fluka 100C8 C1 (60755–50 G). Points — experimental data, solid lines — calculations taking into account the distribution of clusters on the number of pores from [23], dotted line — calculations within the framework of the model, taking into account the local environment of each pores [16,17]](image)

Fig. 3 presents the intrusion-extrusion curves for the porous medium Fluka 100C8 C1 (60755–50 G), obtained at full and partial filling of the porous medium with water at a temperature of 42°C. For two other porous media, similar patterns of intrusion/extrusion are observed and therefore are not given here. The differences between the obtained curves and the Liebersorb-water system intrusion/extrusion curves [6, 16] attract attention. Thus, the filling curve for Fluka after the filling pressure is not a horizontal "shelf" (as in the case of Libersorb23-water system [16,17]), but a slowly increasing function. Also it is essential feature of the received results consists that the share of not leaking liquid is defined by initial filling of a porous medium. Such behavior also differs from the behavior of the Libersorb23-water system, for which the share of the share of nonleaking liquid on the initial degree of filling was a stepwise character [16,17].

It should be noted that at the filling stage, the pressure at which the porous medium begins to fill with a non-wetting liquid does not depend on the initial filling of the porous body. Such an effect is characteristic for systems of nanoporous medium - non-wetting liquid [6] and is connected with physical features of the filling process, which will be discussed below.
The results of the study of relaxation processes of the initial state of the system are presented in Fig. 4–6. All obtained as a result of measuring the dependence of the degree of filling of a porous body on time is characterized by an initial drop in the degree of filling at the times of a few seconds followed by a slow decline in the degree of filling at the times of hundreds of seconds. Interestingly, the characteristic time of the initial rapid-flow stage does not depend on the specific porous medium, temperature and initial filling degree. The proportion of non-outflow liquid depends on both the porous medium and temperature and the initial filling, and the reduction of the initial filling level results in a smooth drop in the volume of non-outflow liquid.

Figure 4. Dependence of the fraction of the filled volume of a porous body Fluka 100C8 C1 water system’s on time. Left panel – 22°C, right panel – 42°C. Points – experimental data, lines – formula calculations 6

Figure 5. Dependence of the fraction of the filled volume of a porous body Fluka 100C8 C1 water system’s on time. Left panel – 22°C, right panel – 60°C. Points – experimental data, lines – formula calculations 6

Figure 6. Dependence of the fraction of the filled volume of a porous body Fluka 100C8 water system’s on time. Left panel – 10°C, right panel – 22°C. Points – experimental data, lines – formula calculations 6
3. Discussion
To describe the processes of intrusion-extrusion of non-wetting liquid from a porous body in the works [5,6] the model based on the theory of percolation and taking into account energy barriers of filling and outflow was proposed. This model was further developed in [16-19,24,25], which allowed, in particular, to reveal the mechanisms of slow liquid extrusion from a porous body. In the present work, the description of the experimental data obtained is carried out within the framework of this model. In accordance with [6], the processes of intrusion and extrusion are considered as a process of interaction of formed percolation clusters available for filling (flowing out) porous medium pores and filled (empty) pores. The portions of $\theta_{in}$ and $\theta_{out}$ available for intrusion and extrusion in the corresponding processes at $p$ pressure are determined by the ratios:

$$\theta_{in} = \int_{n}^{\infty} \frac{4}{3} \pi R^3 f(R) w_{in}(p, R) dR, \quad (1)$$

$$\theta_{out} = \int_{n}^{\infty} \frac{4}{3} \pi R^3 f(R) w_{out}(p, R) dR, \quad (2)$$

where $f(R)$ is unit-normalized pore distribution function by radius, $w_{in}(p, R)$, $w_{out}(p, R)$ are normalized per unit of probability of intrusion and extrusion, respectively. Values $w_{in}$ and $w_{out}$ are determined by the values of the work $\delta A_{in}$ and $\delta A_{out}$ on intrusion and extrusion of liquid from pore radius $R$ from porous medium:

$$\delta A_{in} = -\frac{4}{3} \pi R^3 p + 4 \pi R^2 \delta \sigma (1 - \eta(R)) + 4 \pi R^2 \sigma \eta(R), \quad (3)$$

$$\delta A_{out} = \frac{4}{3} \pi R^3 p - 4 \pi R^2 \delta \sigma (1 - \eta(R)) + 4 \pi R^2 \sigma \eta(R). \quad (4)$$

Here $\sigma$ is surface tension coefficient of non-wetting liquid, $\delta \sigma$ is difference of coefficients of surface tension of liquid-porous medium and gas-porous body interface, $\eta(R)$ is ratio of meniscus area to pore surface area.

The transformation of clusters available for intrusion (extrusion) of pores into clusters of filled (empty) pores, according to the work [6], can be considered as the interaction of these clusters. In this case, the task of describing the intrusion and extrusion processes is to calculate the function of distributing clusters of filled (empty) pores by the number of pores in them. For the case of quasi-static pressure changes, the solution of this problem in the three-dimensional case looks like [21]:

$$F(n, p) = C n^{-\tau} \exp \left(-\frac{\left|\theta_{in} - \theta_{c}\right| n^s}{\theta_{c}}\right), \quad C = \left(\int_{1}^{\infty} F(n, p) \, dn\right), \quad (5)$$

where $\theta_{c}$ is percolation threshold, $\tau$, $s$ are indicators that determine the dependence of the number of clusters on the number of pores in them and the number of pores in a cluster with a characteristic size equal to the correlation length.

Relationships (1)–(5) allow to describe the processes of intrusion/extrusion of a porous body with non-wetting liquid. Fig. 3 shows the calculated dependence of the porous body filling degree on pressure. It can be seen that the calculated dependences describe the experimental data on intrusion and extrusion of water from the porous medium Fluka 100C8 C1 (60755–50 G). Calculations show that the experimental data on two other porous media can also be successfully described using the ratios (1)–(5).

It should be noted that the scaling distribution function of $F(n, p)$ was also used in [5,6]. However, calculations have shown that the use of the scaling distribution function does not allow us to describe the experimental data on the outflow of liquid [6].
Another modification of the model was carried out in [16-19,24,25]. In order to take into account the effects of interaction between clusters of available and filled pores (and available and empty for the case of an outflow), instead of calculating the distribution function $F(n,p)$, it was proposed to calculate the work on filling and leak of fluid from the pores, taking into account the emergence and disappearance of meniscuses in the local environment (in the first coordination sphere) of the pores. Calculations performed in the framework of the present work have shown that this approach is equivalent to the use of scaling distribution function and allows describing only the process of filling the porous body. As shown in Fig. 3, the process of extrusion in such an approach cannot be described - the extrusion pressure is lower than the experimental one, and when the pressure drops below the extrusion pressure, the volume of the fluid outflow is overestimated. This is due to the fact that the long-range interaction between the filled pores in the percolation cluster of pores available for the outflow plays an essential role in the process of outflow. The use of the scaling distribution function, in fact, limits the characteristic area of such interaction to the nearest pore environment, which is similar from the physical point of view to the consideration of the change in the energy of the outflow due to the nearest pore environment, as proposed in [25]. A detailed analysis of the difference between the model based on the distribution function (5) and the model proposed in [25] will be carried out in a separate paper.

To describe the processes of relaxation of the initial state of the system non-wetting liquid-porous body in the works [16-19,24,25] the model was proposed, which is a natural continuation of the above model and is based on obtaining the kinetic equations of relaxation of the functions of distribution of filled and empty pores. In the quasi-equilibrium case, such an approach allowed us to calculate the dependence of the degree of filling of a porous body on time in the process of liquid outflow:

$$\theta(t) \sim \theta_0 \left( \frac{\tau_0}{\tau} \right)^{\alpha}, \quad \alpha = \left( 1 + (2 - \gamma) \frac{\Delta R A_{\text{max}}}{R T} \right)^{-1}, \quad \tau_0 \sim \tau_0 \exp \left( \frac{A_{\text{max}}}{T} \right).$$  

(6)

When calculating the dependence, it was assumed that the function $\eta(R) \sim R^{-\gamma}$, and the value of $A_{\text{max}}$ is the maximum work of the pore outflow, $\theta_0$ is the initial degree of filling, $\tau_0 \sim 0.1$ s is the hydrodynamic time of fluid outflow from the pore, $T$ is the temperature.

Calculations using the ratio (6) allow us to describe the experimental dependence of the degree of filling of a porous body on time (see Fig. 4–6). Within the framework of the model used, both the stage of rapid avalanche outflow under the self-organized criticality scenario and the stage of slow relaxation at long times can be described. Physical reasons for this type of relaxation of the non-wetting liquid porous body can be detected by analyzing the density of energy states of pores [18,19]. Fig. 7 shows the density of energy states of liquid in a porous medium Fluka 100C18 at full filling and temperature of 22° C. It can be seen that some of the states are in the negative region, and therefore are favorable for the outflow, and the time of the outflow of the order of hydrodynamic time $\tau_h \sim 0.1$ s. The presence of such states provides the initial stage of rapid fluid outflow from the porous body under the scenario of self-organized criticality. Calculations show that the density of states of all studied porous media regardless of temperature has a similar form. This explains the first stage of rapid relaxation under the self-organized criticality scenario, which was discovered in experiments.

It should be noted that the studied porous media differ significantly from the previously studied media of the Libersorb23 [1]. Porous media of Fluka type are characterized by a wide distribution of pores in size, while for Libersorb23 the distribution width is much smaller than the average radius. It is this difference that provides for the presence in the initial state of both energetically unfavorable for the leakage states with positive energies, and profitable for the leakage states with negative energy. Porous bodies in which the coexistence of fast and slow states at the initial moment of time is established, are investigated for the first time, separately.
Figure 7. Energy density of fluid clusters in porous medium Fluka 100C18 at full filling at temperature 22°C

note that such a physical picture is observed in all experiments and does not depend on the initial degree of filling of the porous body and temperature.

The experimental data obtained (e.g. hysteresis of intrusion/extrusion) indicate that effective wetting of the liquid in the intrusion/extrusion process has occurred. The above model allows us to offer a microscopic mechanism of effective wetting, which is due to the attraction of fluid clusters in a porous medium. The theoretical model used allows calculating the effective wetting angle taking into account the processes of formation of clusters available at a given pressure and filled pores. The analysis of the dependence of the effective wetting angle on external conditions will be carried out in a separate paper.

4. Conclusions

In the present work we present the results of experimental research and theoretical description of the processes of intrusion-extrusion and relaxation of metastable states of water-porous body systems for three different porous bodies of Fluka. Such porous mediums are characterized by a relatively small value of the average pore radius ($\bar{R} \sim 3.7 \div 3.8$ nm) and a wide distribution of pores in size ($\Delta R/\bar{R} \sim 0.4$). It is shown that these porous bodies are characterized by smooth dependences of the amount of non-outflow liquid on the initial degree of filling, as well as a gradual increase in pressure in the process of filling the porous body. The dependence of the degree of filling of the porous body on the time in the process of extrusion is obtained. For all the examined porous bodies and external conditions the extrusion occurs in two stages. At first, liquid flows out of the porous body according to the scenario of self-organized criticality at the times of about several seconds, after which a slow flow out with a characteristic time of several hundred seconds occurs.

Theoretical description of the obtained dependencies was carried out within the framework of the previously developed models. It is shown that the rapid initial outflow of a non-wetting liquid-porous body in the process of relaxation of the metastable state is conditioned by the presence in the initial energy spectrum of the outflow energies of the liquid state with negative energy, beneficial for the outflow during the hydrodynamic time. After emptying the pores corresponding to the rapid states, the characteristic time of relaxation of the system sharply increases, which causes a slow outflow of liquid at long times.
The analysis of the extrusion process has shown that the amount of outflow liquid is determined not only by the energy state of the pore, taking into account its local environment, but also by long-range interaction in a cluster of pores available for flowing out. Accounting for such interaction is possible by calculating the function of distribution of clusters of pores available for outflow by the number of pores in them. Such an approach allows us to describe the experimentally obtained hysteresis of intrusion-extrusion both in the case of complete primary filling of porous medium and in cases of partial filling. The obtained results indicate the need for additional detailed analysis of the outflow process taking into account the multiparticle long-range interaction. This analysis will be carried out as part of a separate exercise.

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