

# THE DISTRIBUTION OF CAPTURED NON-WETTING LIQUID DISPERSED IN NANOPOROUS MEDIUM RECOVERY METHOD

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**Abstract.** In this paper the recovery method of a distribution function of non-wetting liquid captured in porous medium presented. Computation algorithm described. The recovered distribution functions for the system nanoporous medium (Libersorb 23) - non-wetting liquid (water) at the temperature of experiments 6<sup>0</sup>C presented. The used for calculation experimental data obtained in the time relaxation of metastable states of the non-wetting liquid in a porous medium experiment [Borman et al. 2016 *Phys Rev E* **93** 022142].

## 1. Introduction

The study of non-wetting liquid entrapment phenomenon continuous more than a twenty years [1, 2]. This phenomenon is observed not only for disordered porous media [2], but also for porous media with an ordered structure, such as MCM and SBA type materials [2, 3]. Basic models for describing the process of intrusion - extrusion non-wetting liquid from the pores are models based on the Laplace equation and its modifications [1, 2]. In many models to describe entrapment phenomenon proposed a change in contact angle of wetting or assumption of pore size distribution spatial heterogeneity. Also in recent years have been found such effects during intrusion - extrusion non-wetting liquid process, as the existence of metastable states [4] and their power law relaxation [5]. The effect of pores spatial distribution and its correlation in space can have a significant contribution on the non-outflow phenomenon.

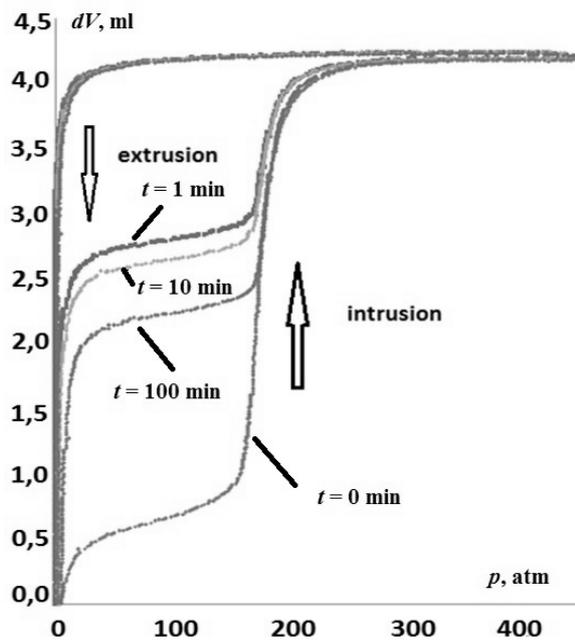
The aim of this work was to develop a method to determine the pore size distribution for pores from which non-wetting liquid does not outflow after reducing the excess pressure to zero. The proposed method allowed us to determine the characteristic size of the pores in assumption of cylindrical pores. Estimates are provided for the relaxation experiments to investigate metastable states Libersorb 23 - water system at a temperature of 6<sup>0</sup>C and observation time 0, 1, 10 and 100 minutes. The calculated pore size distribution functions demonstrate that there is a bimodal distribution of pores from which liquid does not outflow after the decrease excess pressure to zero.

## 2. The Experiment

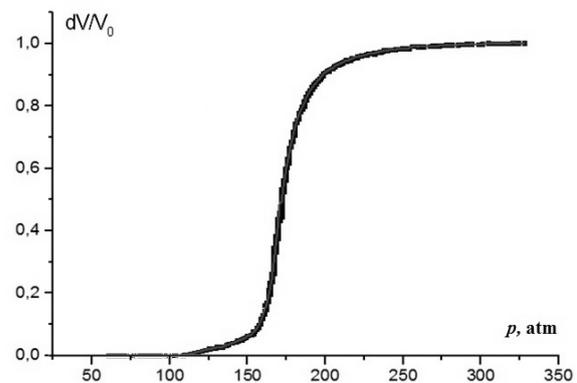
The method has been tested on the experimental results of the metastable states relaxation study presented in [5]. Grafted silica gel Libersorb 23 (L23) as nanoporous medium and water



as non-wetting liquid have been used for study. The characteristics of nanoporous medium and method for obtaining the experimental data described in [5, 6]. The initial experimental data of pressure dependences of a change in the volume of the L23 water system for analysis presented on Fig 1. This is a typical intrusion - extrusion cycles with time delay after the first cycle ( $t = 0$  min) 1, 10 and 100 min. Increasing of time delay increases quantity of non-wetting liquid outflowed from pores and each intrusion curve presents new state of empty pores after extrusion. The data for calculation presented on Fig 2. This data normalized on volume of pores and compressibility of empty porous medium.



**Figure 1.** Dependences of internal camera volume changes with applied pressure for water intrusion - extrusion cycles in nanoporous medium L23 at 6 with time delay 0, 1, 10 and 100 minutes.



**Figure 2.** Normalized experimental data for  $t = 0$  min.

It is well known method pore size distribution function recovery based on intrusion non-wetting liquid in porous medium [7]. Examining of intrusion experiments as independent and the comparison of distribution functions will provide information about the distribution of non-wetting liquid captured in a porous medium.

### 3. The Calculation method

According to the classical method of determining the pore size distribution function  $f(R)$  by mercury porosimetry [7], the recovery of distribution function in the approximation of cylindrical pores of a porous medium, where the relationship between pressure ( $p$ ) and a pore radius ( $R$ ) defined by the Laplace equation  $p = -\frac{2 \cdot \sigma \cos \theta}{R}$ , where  $\sigma$  - liquid surface tension,  $\theta$  - contact wetting angle. Calculation of  $f(R)$  is carried out according to:

$$f(R) = \frac{p^2}{2 \cdot \sigma \cos \theta} \cdot \frac{dV}{dp}, R = -\frac{2 \cdot \sigma \cos \theta}{p}, \quad (1)$$

where  $dV/dp$  - derivative of the experimental dependence of  $dV(p)/V_0$ . Since the experimental methods of obtaining dependencies  $dV(p)/V_0$  in the mercury and water porosimetry are close, the task of restoring the distribution of functions in the approximation of cylindrical pores is reduced to the computation of the derivative  $dV/dp$ , and the definition of the value of  $\theta$ . For derivative  $dV/dp$  initial experimental dependences previously been converted, taking into account the deformation of porous medium, is not filled with the non-wetting liquid, and normalized to the full pores volume  $V_0$ , determined in the first intrusion - extrusion cycle (see fig.2). It was then carried out smoothing the experimental curves. New values of the experimental points ( $V_j = \frac{1}{n} \sum_{i=m}^{i=m+n-1} V_i; p_j = \frac{1}{n} \sum_{i=m}^{i=m+n-1} p_i$ ) at  $n = 5, m = 1 + (j - 1) \cdot n, j = 1, 2, 3, \dots, k$ . Averaging over five points, as subsequent processing steps is optimal. The results before and after the smoothing procedure the same, within measurement error. The next stage of calculation consisted numerical differentiation smoothed experimental dependence. The result of numerical differentiation of the experimental dependence is not a smooth function and as a consequence, the further processing of the results is complicated, because it contains numerous peaks that are artifacts of the numerical differentiation. Also, the presence of a large array of data requires additional software packages for further analysis. Therefore, to optimize the processing techniques, depending on the numerical differentiation obtained were approximated by an analytical function. Preliminary analysis showed that the function:

$$F(x) = \sum_{i=1}^5 \frac{A_i}{w_i \cdot \sqrt{\pi/2}} \exp \left[ -2 \left( \frac{x - \bar{x}_i}{w_i} \right)^2 \right], \quad (2)$$

with reliability  $R^2 \geq 0.998$  approximates the obtained numerical dependence. Increasing the number of functions more than five ( $i > 5$ ) does not increase reliability  $R^2$ , but fewer functions ( $i < 5$ ) can not achieve  $R^2 \approx 1$ . The correctness of approximating function choice (2) has been proofed by the integration and comparison to the original experimental data according to:

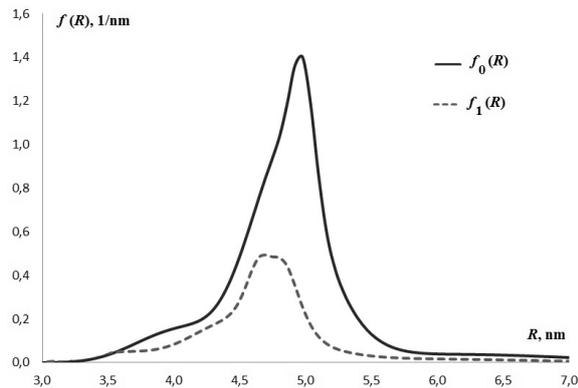
$$\int_{50}^a F(x) dx, \quad (3)$$

where the upper limit of integration  $a = 50 \div 350$  atm, and  $x$  is replaced by the pressure  $p$ . The obtained calculation of the approximation function according to (3) describes the experimental data within measurement error. Thus, this method of calculation allows high accuracy to determine the analytical form of the derivative  $dV/dp$  and use this function in subsequent calculation. Figure 3 shows two pore size distribution functions calculated by the above-mentioned methods in accordance to the equation (1) there  $dV/dp = F(x)$  for the system L23 water at a temperature  $6^0\text{C}$ . The contact Angle is determined from the work [3] and is equal to  $124^0$ .

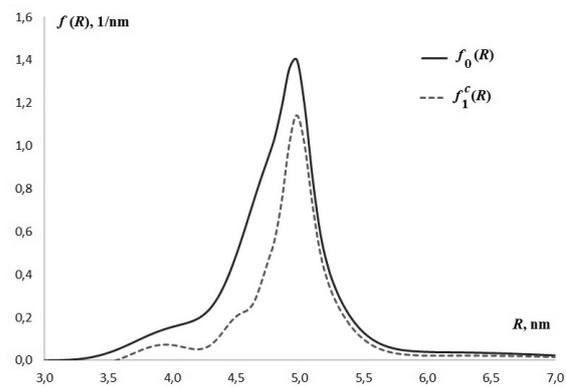
As it seen from figure 3, the distribution function of pore size after a time delay of  $t = 1$  min  $f_1(R)$  is below the distribution function  $f_1$  obtained from the experimental data in terms of the empty porous medium  $f_0(R)$  in the whole range of radii. Thus, the pore size distribution function of a porous medium filled non-wetting liquid can be defined as the difference between the two distribution functions:

$$f_1^c(R) = f_0(R) - f_1(R). \quad (4)$$

The result of subtraction according to 4 for pore size distribution function  $f_1^c(R)$  at 1 minute time delay and pore size distribution function of the empty porous medium  $f_0(R)$  are presented on figure 4. As an additional check, we calculated the definite integral of a function  $f_1^c(R)$ . The value obtained within the measurement errors consistent with the part of liquid captured in the porous medium.



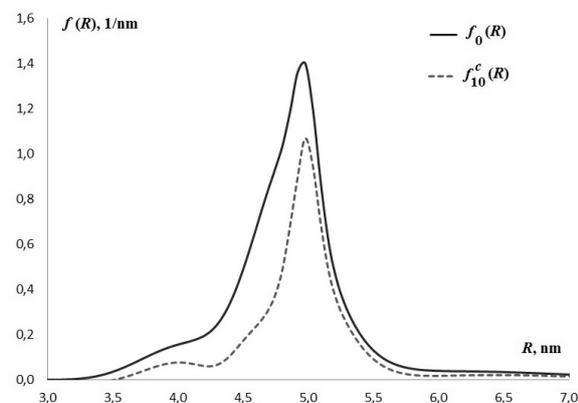
**Figure 3.** The distribution function obtained from the experimental data in terms of the empty porous medium  $f_0(R)$  and  $f_1(R)$  the distribution function of pore size after a time delay of  $t = 1$  min .



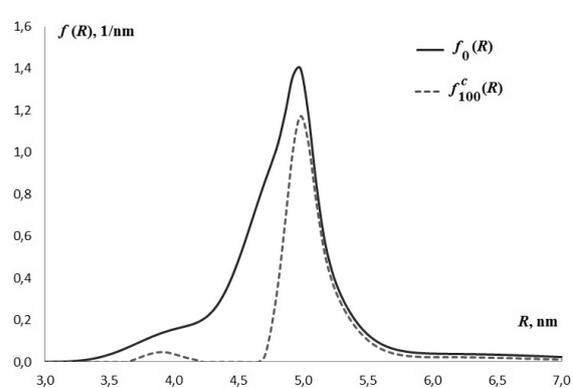
**Figure 4.** The pore size distribution function of pores filled by non-wetting liquid  $f_1^c(R)$  with 1 minute time delay and pore size distribution function of the empty porous medium  $f_0(R)$ .

#### 4. Results

In accordance to the procedure described above were also obtained pore size distribution functions of pores filled by non-wetting liquid at time delay 10 and 100 minutes, respectively. The results are shown on Figures 5 and 6. Also on the figures, for comparison, the pore size distribution function  $f_0(R)$  presented.



**Figure 5.** The pore size distribution function of pores filled by non-wetting liquid  $f_{10}^c(R)$  at 10 minutes time delay and pore size distribution function of the empty porous medium  $f_0(R)$ .



**Figure 6.** The pore size distribution function of pores filled by non-wetting liquid  $f_{100}^c(R)$  at 100 minutes time delay and pore size distribution function of the empty porous medium  $f_0(R)$ .

As seen from Figures 4 - 6, the amount of liquid in the porous medium decreases with increasing time between cycles. The distribution function then the liquid is not outflow after reducing the excess pressure to zero is changing. The fluid does not flow out of the pores of large and small size and bimodal distribution occurred. The magnitude of peaks with increasing time delay decreases, which corresponds to an increase of the amount of liquid flowing out of the pores at time delay increase. Also, it can be assumed on the spatial heterogeneity of the

pore distribution. Bimodal distribution may be indicative of the spatial configurations existence, where a large pores are surrounded by a smaller ones.

## 5. Conclusion

We propose a method of recovering pore distribution function of a porous medium filled with the non-wetting liquid. We obtain the distribution function of captured liquid for experiments to investigate the relaxation of non-wetting liquid (water) in a porous medium (L23) at a temperature of 6<sup>0</sup>C. It is shown that the distribution function is bimodal. Assumed that this type of function may be due to the spatial heterogeneity of pores and in the existence of spatial configurations, where large pores are surrounded by small pores.

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