Study of local configurations in the systems “disordered nanoporous medium – non-wetting liquid”

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Abstract. The analysis of redistribution functions of non-wetting liquid (water) dispersed in disordered nanoporous media of Libersorb 23, obtained in work [22]. Local configurations which describe the time relaxation of a non-wetting liquid dispersed in a disordered nanoporous medium are studied. It is shown that various possible local configurations can be used to describe the temporal relaxation of a liquid dispersed in a nanoporous medium. A qualitative picture is presented of the possible mutual arrangement of the pores in the porous medium Libersorb 23. The presented approach allows qualitatively to restore the spatial distribution of pores of a porous medium.

1. Introduction

The problem of the relaxation of metastable states in disordered media such as glasses, colloids, and polymers is one of the most urgent problems for both theoretical and experimental physics [1-15]. It was shown that the state of such media is nonergodic and their relaxation is described by the law of a prolonged exponential [3, 11, 15]. For the description of states and relaxation of glasses, colloids and polymers, the concept of local structures is used in such models as shear transformation zone (STZ), dynamic heterogeneity (DH), and random first order transition theory (RFOT) [4, 7, 8].

At the same time, the applied meaning of solving the relaxation problem is important for the industry, since porous media, mainly disordered media, are widely used in such processes as catalysis, filtration [16, 17]. In addition to the interest in the study of the relaxation of porous media, there is the problem of the spatial arrangement of pores in a porous medium, since knowledge of such structural characteristics of the medium as pore size distribution and connectivity is often insufficient for predicting processes in porous media [18, 19]. For example, for heat and mass transfer during the flow of gases and liquids in porous media, determination of flow velocity, temperature and pressure [20]. Anomalously slow relaxation of a non-wetting liquid in a disordered nanoporous medium [21] and method of restoring the distribution function of a non-wetting liquid dispersed in a nanoporous medium [22] can be used to create a technique for restoring the spatial distribution of pores in a porous medium. Anomalously slow relaxation implies that limited fluid clusters can be located inside the pore space for long periods of time, and can indicate the existence of certain local pore configurations (some spatial arrangement of the pores). The spectrum of the relaxation times of metastable states was
calculated in work [23]. It was also shown there that the relaxation of metastable states is described by a power law. In this case, a quantitative analysis of the dispersed non-wetting liquid will allow to determine the most probable configurations and estimate their number.

The presented results of the analysis of the redistribution functions of a non-wetting liquid dispersed in a disordered nanoporous medium of Libersorb 23 (L23), obtained in work [22] show, that various possible local configurations can be applied to describe the temporal relaxation of a liquid dispersed in a nanoporous medium. It is also shown, that the proposed analysis can be the basis for a technique for determining the spatial distribution of pores of a porous medium that can be described by various local configurations.

2. Methods and materials

The observation of local configurations in the system disordered nanoporous medium – non-wetting liquid was carried out according to the experimental data for the system L23 – distilled water [24]. The porous medium L23 is the hydrophobized silica gel KSK-G. This sample has characteristics: skeleton density \( \rho = 1.7798\pm0.0016 \text{ g/cm}^3 \), specific pore volume \( V_p = 0.62\pm0.02 \text{ cm}^3/\text{g} \), porosity of the material \( \phi = 0.52 \), surface area \( S_p = 199\pm7 \text{ m}^2/\text{g} \), average granules size \( \sim 10 \mu\text{m} \), average pore radius \( \langle R \rangle = 5.0\pm0.2 \text{ nm} \). Method of obtaining this material and its characteristics described in detail in the work [21].

Results of research on the process filling porous medium by non-wetting liquid and process outflow of non-wetting liquid from the porous medium in quasistatic pressure change were obtained at the experimental installation. Data were obtained according to the method of measuring the time relaxation of non-wetting liquid dispersed in a nanoporous medium. Experimental installation and measuring techniques described in work [25]. The results were obtained for the following experimental conditions: nanoporous medium weight – 4 g, volume of liquid – 55 cm³, temperature – 6, 9, 16 °C and time interval between infiltration-defiltration cycles – 1, 10, 100 minutes.

The analysis of the experimental data was carried out in accordance with method of restoring the distribution function of non-wetting liquid dispersed in the pores of the porous medium, after reducing the excess pressure to zero [22]. The basis of this method is to compare the functions of empty pores for different time delay after the reduction of the excess pressure to zero. Main processing points:

1. Deduction from the data of the change in the volume of the system associated with elastic deformation;
2. Normalization of experimental data by volume on the total pore volume in the first experiment;
3. Smoothing of the obtained experimental data by averaging over five points;
4. Comparison of processing results with experimental data taking into account the measurement error;
5. Numerical differentiation of data after processing;
6. Approximation of the obtained data by the analytic function. This function is the sum of five Gauss distribution functions and ensures the reliability of the approximation \( R^2 \geq 0.998 \);
7. Integration of an analytic function and comparison with experimental data.

As a result, derivatives were obtained for the experimental set of points in the analytical form. The distribution function of a non-wetting liquid dispersed in porous of media in terms of pore sizes was determined as:

\[ f'_t(P) = f_0(P) - f_t(P), \]

were \( f_0(P) \) - function of the distribution of the pore volume in terms of the sizes available for the liquid at the initial instant of time, \( f_t(P) \) - function of the distribution of the pore volume in terms of the sizes available for liquid after the waiting time \( t \) after filling. The result of calculating the total integral for the obtained distribution function of a non-wetting liquid dispersed in a nanoporous medium gives a value equal to the fraction of the non-wetting liquid from the pore space.

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3. Results
We consider in detail the results obtained for 6°C. The results of calculating the distribution of non-wetting liquid dispersed in a nanoporous medium, according to the described procedure [22], shown in the figure 1a. The figure shows the presence of a peak in the region of small pores (~4 nm) and pronounced peak in the region of large pores (~5 nm). According to the distribution of liquid dispersed in a nanoporous medium at full filling (figure 1a, solid line) will outline the main pore sizes: large pores (~5 nm), pores of medium size (~4.5 nm) and small pores (~4 nm). Their volume fraction accordingly is 70, 20 and 10% of the total volume. In work [21] was shown, that for medium L23 the characteristic number of nearest neighbors for a given pore is 4-6 and porosity \( \varphi = 0.52 \). To estimate the probability of neighborhood of pores of different sizes, we use formula [26]:

\[ P(\theta) = \theta_1 \times \theta_2 \]

were \( \theta_1 \) and \( \theta_2 \) - fraction of pore volume with a given radius of the total pore volume. Probability of pore space “small-small” is 0.01; probability of “small-large” is 0.07; probability of “large-medium size” is 0.14; probability of “small-medium size” is 0.03; probability of “large-medium size” is 0.49. According to estimates, nanoporous medium L23 is a cluster of large pores surrounded around the perimeter of mostly small pores. On the figure 1b shown qualitatively section possible arrangement of clusters.

Let us consider the distribution of a liquid dispersed in a nanoporous medium 1 minute after full filling (see figure 1a) dot-dash line. The figure shows a decrease in volume over the entire range of pore sizes. Most of the liquid remains in large pores (~5 nm). Also, there is a seizure of liquid in pores of medium size (~4.5 nm) and small pores (~4 nm). Such a distribution may correspond to the picture in the figure 1b. Here the liquid filled pores are shown in blue, and white - empty pores. Cluster of non-filling 1 in the Figure 1b corresponds to a peak in the region of large pores (~5 nm). In Figure 9a, the dashed-dot line shows the distribution of the non-filling liquid 10 minutes after full filling and the reduction of the excess pressure to zero. It can be seen that a decrease in the volume of non-filling occurs in the pore area of medium size (~4.5 nm), slightly decreases in the region of large pores (~5 nm), and in the region of small pores (~4 nm) there is no change in comparison with the distribution after 1 minute. The possible distribution of the non-filling liquid is shown in Figure 9b. Here the blue color shows pores filled with liquid, and white - empty pores. The cluster of non-filling liquid 1 corresponds to a peak in the region of large pores (~5 nm). Cluster 2, shown in Figure 1b, corresponds to the pores of large (~5 nm) and medium (~4.5 nm) sizes disappear.

Consider the distribution of the non-filling liquid dispersed in a nanoporous medium 100 minutes after filling (see Figure 3a). The dotted line shows the distribution of the non-filling liquid dispersed in a nanoporous medium 100 minutes after full filling and reducing the excess pressure to 0. The figure shows that the liquid as well as for 10 minutes does non-outflow of large pores (~5 nm). It flows from pores of medium size (~4.5 nm), and partly from small pores (~4 nm). A possible picture of the location of clusters of non-filling liquid is shown in Figure 3b. Where blue is filled pores, and white - empty pores. Cluster 1 in Figure 3b corresponds to peaks in the region of large pores (~5 nm) and in the region of small pores (~4 nm).

Thus, the assumption of the arrangement of small pores (~4 nm) along the perimeter of the large-pore cluster is completely within the framework of the result obtained. The flow of medium pores (~4.5 nm) and small pores (~4 nm) observed after 100 minutes can be explained by the assumption that small pores located along the perimeter of the cluster are connected with a large-pore cluster through pores of medium size.
Figure 1a. The pore size distribution function of pores filled non-wetting liquid (solid line); distribution of pores filled with liquid for 1 minute time delay (dot-dash line).

Figure 1b. The qualitative distribution of the liquid of the remaining porous medium in space after 1 minute time delay. In blue - filled pores, white - empty pores.

Figure 2a. The pore size distribution function of pores filled non-wetting liquid (solid line); distribution of pores filled with liquid for 10 minutes time delay (dot-dash line).

Figure 2b. The qualitative distribution of the liquid of the remaining porous medium in space after 10 minutes time delay. In blue - filled pores, white - empty pores.
Figure 3a. The pore size distribution function of pores filled non-wetting liquid (solid line); distribution of pores filled with liquid for 100 minutes time delay (dot-dash line).

Figure 3b. The qualitative distribution of the liquid of the remaining porous medium in space after 100 minutes time delay. In blue - filled pores, white - empty pores.

4. The discussion of the results
Consider the redistribution of liquid at 60°C. According to the figures 1b – 3b, the non-wetting liquid in the pore space forms certain local configurations. Examples of such possible local configurations are shown in Figure 4. Figure 4 is represent section of porous media. For given local configurations, we estimate the energy and time of fluid flow from a given pore.

Figure 4. A qualitative picture of the mutual arrangement of the pores of a porous medium L23 with isolated local configurations.

Consider a possible local configuration representing a small pore surrounded by four large. In Figure 14, it is denoted by 1. We estimate the energy of a given small pore (~ 4 nm). According to the work [27], the change in the surface energy $\Delta E$ of the liquid in the pore is described as:

$$
\Delta E = \Delta E_s + \Delta E_I
$$

Where $\Delta E_s$ - is the change in the surface energy at the solid-liquid interface, and $\Delta E_I$ - is the change in the surface energy at the liquid-gas interface. According [27], connection between energy and characteristics of a porous medium and a liquid: $\Delta \sigma$ - the change in the specific energy of the surface of a solid with the outflow of liquid, $s$ - pore surface area, $s_m$ - surface area of the meniscus, $z$ - number of pores – neighbors, $n$ - number of filled pores – neighbors, is defined by the equation:
\[ \Delta E_s = -\delta \sigma (s - s_m z) \]  
\[ \Delta E_l = \sigma s_m (2n - z) \]  

Flow is possible if \( \Delta E < 0 \). For the given pore, \( \Delta E > 0 \) if \( n = 3 \). Then the pore is in the filled state. The time for the outflow of liquid from the pore is determined by the relation:

\[ \tau = \tau_0 \exp(\delta A / T) \]  

(4)

Were \( \tau_0 \approx 10^{-11} \) s - characteristic hydrodynamic flow time of the fluid in the experiment, and \( \delta A = pV + \Delta E \) - work that is needed to spend on outflow liquids from the pores. In the absence of excess pressure in the system (\( p = 0 \)), \( \delta A = \Delta E \). For a local configuration, a small pore with three filled neighbors of four \( n = 3 \), which exceeds the experimental observation time (\( 6 \times 10^3 \) s).

We also estimate the leak time for a possible local configuration indicated in Figure 4 the number 2. It is a large pore (~ 5 nm), surrounded by 5 neighbors. For a given pore, with 4 empty of 5 neighboring pores, it is estimated that the time \( \tau \approx 4 \times 10^8 \) s, hat exceeds the time in the experiment. Consider the local configuration 3 (Fig.14), which is a given time of average size (~ 4.5 nm) with six possible neighbors. The time estimate, according to the formulas (1-4), with 4 occupied neighbors of 6 gives the value \( \tau \approx 3 \times 10^5 \) s, which exceeds the experimental observation time (\( 6 \times 10^3 \) s).

Another possible local configuration is shown in Figure 4 under number 4. It is a given large pore (~ 5 nm) with 2 possible neighbors. Provided that all 2 neighbors are in the filled state, \( \tau \approx 4 \times 10^2 \) s.

Figure 4 shows the local configuration at number 3. It is a time of medium size (~ 4.5 nm), with 5 neighboring pores. In the case that 4 out of 5 neighbors are in a full state, the time \( \tau \approx 5 \times 10^3 \) s, which corresponds to the observed outflow at times of 100 minutes.

The obtained estimates of the fluid outflow time for certain local pore configurations can be correlated with the theoretical description of the relaxation of a non-soaking non-wetting liquid obtained in [28], as a function of time. Figure 5 shows the specific local corresponding to the specific local pore configurations described above.

![Figure 5](image)

**Figure 5.** Qualitative depending of the volume fraction remaining liquid on time and local configurations.
For example, region 1 in Figure 5 can correspond to local configurations: a medium-sized (~ 4.5 nm) area with 6 possible neighbors with 4 occupied neighbors of 6. A region 2 can correspond to a large pore (~ 5 nm) with 2 possible neighbors with 2 filled. Area 3 corresponds to the pore of medium size (~ 4.5 nm), with 5 possible neighbors with 4 filled out of 5. Region 4 corresponds to a pore of small size (~ 4 nm) with 4 neighbors at 1 filled from 4. The obtained calculated values are qualitatively consistent with the results of the theoretical description.

5. Conclusion
On the basis of the functions of the distribution of a non-outflow liquid from pores by the size obtained in [22], an assumption was made about the possible mutual arrangement of the pores in a porous medium. Received qualitative the picture of the mutual arrangement of the pores. The evaluation of the times of non-wetting liquid from the given local configurations was presented. Experimental data of the dependence of a non-wetting liquid, dispersed in a nanoporous medium on time was correlated with theoretical description, presented in work [28].

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References
[1] Falk M L and Langer J S 2011 Ann. Rev. Cond. Matt. Phys.2353.
[2] Bouchbinder E and Langer J S 2009 Phys. Rev. E 80 031138.
[3] Langer J S 2012 Phys. Rev. E 85 051507.
[4] Langer J S 2013 arXiv:1308,6544v2
[5] Bouchbinder E and Langer J S 2011 Phys. Rev. Lett.106 148301.
[6] Borman V D, Belogorlov A A, Grekhov A M and Tronin V N 2014 Eur. Phys. J. B 87 249.
[7] Biroli G and Garrahan J P 2013 J. Chem. Phys.138 12A301.
[8] Dynamical Heterogeneities in Glasses, Colloids, and Granular Media 2011 ed L Berthier, G Biroli, J P Bouchaud, L Cipelletti and W van Saarloos Int. Ser. Monogr. Phys.150
[9] Berthier L and Biroli G 2011 Rev. Mod.Phys.83587.
[10] Chander D and Garrham J P 2010 Ann. Rev. Phys. Chem.61 191.
[11] Potuzak M, Welch R C and Mauro J 2011 J. Chem. Phys.135214502.
[12] Tanaka H, Kawasaki T, Shintani H and Watanabe K 2010 Nat. Mater.9324.
[13] Borman V D, Belogorlov A A and Tronin V N 2015 Phys. Proc.724-9
[14] Rigby S P and Edler K J 2002 J. Coll. Int. Sci.250175.
[15] Phillips J S 1996 Rep. Prog. Phys.591133.
[16] Steefel C, Depaolo D and Lichtner P. 2005 Earth and Plan. S. Lett.,240(3-4):539–558.
[17] Wood B.D., Radakovich K. and Golfer F.. 2007 Adv in Water R,30(6-7):1630–1647
[18] Iliev Oleg, Lakdawala Zahra, et. all 2017 Math. Mod. and Analysis, 671-694.
[19] Raoof A., Hassanizadeh S.M. and Leijnse A.. 2010 Upscaling.Vadose Zone J 9(3):624–636,
[20] Meyers J.J., Nahar S., et. all, 2001 J of Chr. A, 907 57–71.
[21] Borman V D et al 2015 J. Exp. Theor. Phys. 148(6), 1169
[22] Belogorlov A A, Borman V D, et al., 2016 J. Phys.: Conf. S. 751(1), 012030
[23] Borman V D, Belogorlov A A, Byrkin V A and Tronin V N 2013 Phys. Rev. E 88 052116
[24] Borman V D, Belogorlov A A and Tronin V N 2016 Phys. Rev. E 93 022142
[25] Borman V D, Belogorlov A A, Grekhov A M et. all , 2005 J. Exp. Theor. Phys. 127(2), 431
[26] Grinchuk P and Rabinovich O 2003 J. Exp. Theor. Phys.96 301.
[27] Borman V D, Belogorlov A A, Byrkin V A, Tronin V N and Troyan 2013, JETP 144, 1290
[28] Borman V D and Tronin V N, 2016 J. Phys.: Conf. S. 751, 012034