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Observation of relaxation of the metastable state of a non-wetting liquid dispersed in a nanoporous medium

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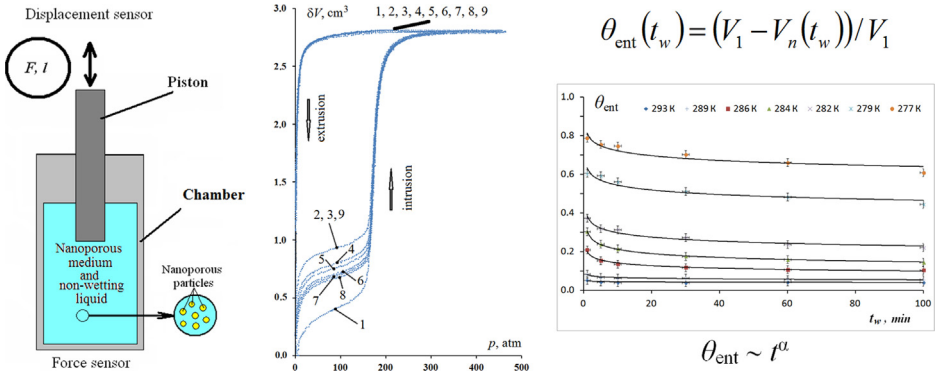
HIGHLIGHTS

- The relaxation of the confined dispersed liquid is observed in the system consisting of water and the three grafted disordered nanoporous media Libersorb 23, Fluka 100 C18 and Fluka 100 C8.
- It is found that the relaxation of these states for the systems under study is anomalously slow, according to an inverse power law with the exponent α.
- The observed anomalously slow relaxation confirm the correctness of the description of disordered media on the basis of the notion of local metastable structures.

GRAPHICAL ABSTRACT



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ABSTRACT

The disordered system of pores in a random nanoporous medium can be filled with a non-wetting liquid at excess pressure. It has been established that, when the porous medium is completely filled and excess pressure is then removed, a part of the liquid can remain in the disordered porous medium. This means that the state of the confined non-wetting liquid is an effectively "wetting" (metastable) state in the disordered confinement of the porous medium. The metastable state relaxation of the confined non-wetting liquid dispersed in the disordered nanoporous medium has been experimentally observed for systems consisting of water and grafted silica gels. In this work, time and temperature dependences of the volume fraction of the non-wetting liquid dispersed in the nanoporous medium have been obtained for three grafted nanoporous media (Libersorb 23, Fluka 100 C18 and Fluka 100 C8) with different pore size distribution functions (PSDs). It has been shown that the PSD, (liquid–grafted solid surface) interaction and temperature strongly affect the experimental dependences obtained. The time dependences of the volume fraction of the non-wetting liquid have been approximated by power law functions for different temperatures. The volume fraction of the confined liquid decreases in time according to a power law as was predicted in [V.D. Borman et al., Phys. Rev. E **88**, 052116 (2013)]. Thus, the observed relaxation of the metastable state can be described as a discrete equilibrium process with the overcoming of numerous local maxima appearing because of random local configurations of filled and empty pores with various sizes in the disordered porous medium.

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1. Introduction

The disordered system of pores in a random nanoporous medium can be filled with an incompressible liquid at a pressure that can be estimated by the Laplace formula. It was established in [1,2] that, when a certain critical degree of filling is achieved and excess pressure then removed, a dispersion transition occurs and a part of the liquid can remain in the disordered porous medium. This means that the confined non-wetting liquid is effectively in a «wetting» state in the disordered confinement of the porous medium. By varying the degree of preliminary filling of the system of pores, it is possible to change ensembles of pores in the bulk of the random medium in which the liquid is confined [1,3]. Confinement of the non-wetting liquid observed as a part of the liquid remaining in the porous medium after its filling [4–13].

Within the consistent statistical description and analytical theory of percolation [14], the extrusion-time distribution of clusters of the confined liquid in pores for the ground state with a fractal percolation cluster was calculated in [3], where a power law of a decrease in the volume of the confined liquid with time was predicted. According to [3], relaxation is a discrete equilibrium process with the overcoming of numerous local maxima appearing because of random local configurations of filled and empty pores with various sizes in the disordered medium. The relaxation of metastable states of the confined liquid has not yet been studied experimentally, but the anomalously slow extrusion of a non-wetting liquid from a porous medium, e.g., mercury from porous glass, was observed [15–17]. It was established that the volume of the confined liquid depends on the temperature, observation time, and sizes of granules of the porous medium [17–19].

The practical interest for the relaxation of metastable states of the non-wetting liquid dispersed in the disordered porous medium is due to using (non-wetting liquid–nanoporous medium) systems in devices for accumulation or dissipation of mechanical energy [20–22]. This effect can also be used for temperature and time dependent processes such as drug extraction from a porous medium.

In this work, the relaxation of the confined dispersed liquid is observed for the system consisting of water and three grafted disordered nanoporous media: Libersorb 23(L23), Fluka 100 C18, and Fluka 100 C8. Metastable states of the dispersed liquid in these systems were revealed in [1,2,23]. According to [2,3,23], one of them, quasi-ergodic, appears through the formation of local configurations of filled pores belonging to the percolation cluster and empty pores separated by a finite potential barrier from the state of the empty medium. The other state, nonergodic, is formed owing to the decay of the fractal percolation cluster of filled pores into individual clusters of filled pores; this decay results in the disappearance of paths for the liquid extrusion through this percolation cluster.

It is found that the relaxation of these states for the systems under study is anomalously slow: it occurs according to an inverse power law with the exponent α. It is also established that the exponent in this law in the temperature range under investigation for the water–L23 system has a minimum, which can indicate a transition from the regime of the accelerated decay of the quasi-nonergodic state with an increase in the temperature to the regime of the decay of the nonergodic state with its slowing down because of the breaking of paths for the escape of the liquid. For the water–Fluka 100 C8 system, the exponent is $\alpha \sim -10^{-4}$ in the whole investigated temperature range. This means that the relaxation time of this metastable state is extremely long. However, the exponent α for the water–Fluka 100 C18 system decreases with an increase in the temperature. The observed anomalously slow relaxation of such systems and comparison with the time dependence of the volume of the confined liquid obtained in [3] confirm the correctness of the description of disordered media on the basis of the notion of local metastable structures.

Table 1
Characteristics of the porous media under study

	Fluka 100 C8	Fluka 100 C18	L23 (C8)
ρ, g/cm^3	1.7603 ± 0.0034	1.6125 ± 0.0025	1.7798 ± 0.0016
V_p, cm^3/g	0.56 ± 0.02	0.46 ± 0.02	0.66 ± 0.02
S_p, m^2/g (BET)	267 ± 10	183 ± 6	212 ± 7
$\phi = V_p/(V_p + 1/\rho)$	0.49 ± 0.02	0.42 ± 0.02	0.66 ± 0.02

2. Materials

The nanoporous media under study were commercially available silica gels with a random structure of pores obtained in the sol–gel process. One of them, Libersorb 23 (L23), was modified in the laboratory headed by Prof. G.V. Lisichkin for obtaining the hydrophobized surface of pores. The other two were Fluka 100 C8—Silica gel 100 C_8, Reversed phase (Sigma–Aldrich catalogue # 60759) and Fluka 100 C18—Silica gel 100 C_{18}, Reversed phase (Sigma–Aldrich catalogue # 60756). Using the pycnometry (micro-Ultrapyc 1200e, Quantachrome Instruments) and porometry (Nova 1200e, Quantachrome Instruments) methods [24], we determined the density (ρ), specific surface area (S_p), specific volume of pores (V_p), and pore size distribution by the classical Barrett–Joyner–Halenda (BJH) method within the cylindrical model of pores and porosity (ϕ) of these materials. The PSDs obtained provide only a qualitative representation of the pore radius distirbution.The results are presented in Table 1 and Fig. 1.

The PSDs of Fluka 100 C8 and Fluka 100 C18 are similar, but the numbers of large and small pores in Fluka 100 C8 are larger than those in Fluka 100 C18. It is possible to deal with the length of a modificator [25]. The PSD of L23 is narrow and this porous medium is more monoporous.

2.1. Measurement procedure

The aim of the performed measurements was to determine the time dependence of the volume fraction of pores θ_{ent} filled with the confined liquid. The confined liquid is defined as the fraction of the liquid that remains in pores after the complete filling of pores at an increase in the pressure and the subsequent removal of excess pressure. The other fraction of the liquid in pores flows from pores rapidly in the pressure decreasing time. The extrusion time of this fraction of the liquid from the L23–water system is smaller than 1 s [26].

The method used to measure the volume of the (non-wetting liquid-porous medium) system was similar to mercury [24] or water [27] porometry. A preliminarily dried and degassed sample of the porous medium with the mass up to 6 g in a container permeable for water was placed in a high-pressure chamber. The remaining free volume of the chamber (28 cm^3) was completely filled with degassed and distilled water. A piston was introduced into the chamber through seals. The chamber was equipped with a thermostating system, which allowed studies in the temperature range from 243 to 393 K. Before the measurements, the prepared chamber was thermostated at a given temperature for no less than 1 h. The temperature in the process of measurements was maintained with an accuracy of 0.2 K. The chamber was mounted on the bench described in [6]. The bench provided controlled force application to the piston of the chamber, measurement of the force, and displacement of the piston. Pores of the porous medium were

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