

Monitoring local configuration and anomalously slow relaxation of a nonergodic system of interacting liquid nanoclusters in a disordered confinement of a random porous medium

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Abstract. The relaxation of a confined nonwetting liquid dispersed in a disordered nanoporous medium has been experimentally studied in the system consisting of water and the L23 hydrophobized silica gel. Discovered that the relaxation of these states to study the system occurs as a result of the relaxation of local metastable configurations of filled and empty pores of the porous medium. Such relaxation occurs abnormally slowly back to the power law with the exponent $\alpha < 0.16$. The observed anomalously slow relaxation of such a system and comparison with the time dependence of the volume of the confined liquid obtained in confirm the correctness of the description of disordered media on the basis of the notion of local metastable structures.

1. Introduction

The disordered system of pores of 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 the excess pressure is then removed, a dispersion transition occurs and a part of the liquid can remain in the disordered porous medium. This means that the confined nonwetting liquid is effectively in a wetting state in the form of an ensemble of liquid nanoclusters 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 nonwetting liquid is observed as a part of the liquid remaining in the porous medium after its filling [4–13]. As a result of the relaxation process, a transition occurs from the nonergodic metastable state of the ensemble of liquid nanoclusters in pores of the disordered medium to the ergodic state of the empty porous medium immersed in the liquid. The porous medium studied in [1, 2] is a silica gel that is obtained in the sol–gel process of formation of the random medium.

The states and properties of disordered media such as glasses, colloids, polymers, and loose media have been actively studied in recent years [14–45]. In the absence of the consistent inclusion of metastable multiparticle correlations, numerical studies were performed and phenomenological models such as shear transformation zone (STZ), dynamic heterogeneity (DH), and random first order transition theory (RFOT) were introduced and discussed (see, e.g., [17, 21, 22]). These models involve the notion of local structures and are used to describe states and relaxation of glasses, colloids,



polymers, and loose media, as well as liquid–glass transitions and sol–gel process, which result in a random order. The state of these media is nonergodic; these media are characterized by the anomalously slow relaxation of nonequilibrium states, which is usually described by a stretched exponential (stretched-exponential relaxation) [18, 28, 34]. In the case of metastable states, typical of the average relaxation time becomes konechnym, while remaining large.

Anomalously slow relaxation means that a system cannot reach any point of the phase space in any large observation time [17,45]. Anomalously slow relaxation is attributed in phenomenological models to the assumed existence and decay of metastable states of random local structures in a disordered medium and to the energy distribution of these states.

Within the consistent statistical description and analytical theory of percolation [41], the escape-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 condition of the trapped non-wetting fluid (water) in the pores was studied by various methods, such as high-resolution quasielastic neutron scattering[36].The relaxation of the metastable states of the confined liquid has not yet been studied experimentally, but the anomalously slow escape of a nonwetting liquid from a porous medium, e.g., mercury from porous glass, was sometimes observed [37,38]. It was established that the volume of confined liquid depends on the temperature, observation time, and sizes of granules of the porous medium [38–40]. The characteristic relaxation (escape) time of a part of the liquid (water in the L23 porous medium) that is not in the confined (metastable) state after filling and removal of excess pressure is 0.1 s at temperatures from 279 to 323 K [42].

In this work, the relaxation of the confined dispersed liquid is observed in the system consisting of water and the L23 hydrophobized silica gel, which is a disordered nanoporous medium. Two metastable states of the dispersed liquid in this system were revealed in [1, 2]. According to [2, 3], 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 escape of the liquid through this percolation cluster.

In the present work found that the relaxation of these states to study the system occurs as a result of the relaxation of local metastable configurations of filled and empty pores of the porous medium. Such relaxation occurs abnormally slowly back to the power law with the exponent $\alpha < 0.16$. The observed anomalously slow relaxation of such a system 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.

2. Main part

The nanoporous medium under study was the commercially available KSK-G silica gel with a random structure of pores obtained in the sol–gel process. Using the porometry and pycnometry methods, we determined the parameters of the resulting Libersorb 23 (L23) porous medium: density $\rho = 1.7798 \pm 0.0016$ g/cm³, specific surface area of pores $S = 212 \pm 7$ m²/g, and specific volume of pores $v = 0.62 \pm 0.02$ cm³/g. The pore size distribution appeared to be close to a Gaussian distribution with the mean radius $\bar{R} = 5.0 \pm 0.2$ nm and the relative FWHM $\Delta R / \bar{R} = 0.07$.

The aim of the performed measurements was to determine the time dependence of the volume fraction of pores θ 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 [35,42]

In our experiments, we used deaerated distilled water (28 ml) and 5 g of this porous medium, which were placed in a high-pressure chamber described in [6,43]. To maintain and measure excess pressure p , to measure change in the volume ΔV of the system at the intrusion–escape of the liquid from pores, and to maintain and measure the temperature, we used the bench described in [6,43]. Measurements of $\theta(t)$ have been performed at each point and each temperature several times.

The measurements showed that the relative volume of liquid $\theta_2 = \frac{\Delta V_2}{V_{pore}}$ remaining after the preliminary filling of the porous medium the relative volume $\theta_1 = \frac{\Delta V_1}{V_{pore}}$ of the liquid depends on the size θ_1 . These dependences are obtained when increasing the system pressure for 15 seconds before filling fraction of the pores θ_1 , the subsequent reduction of the overpressure to zero for 15 seconds and after a timeout of 1 min according to the methods described in [2, 43]

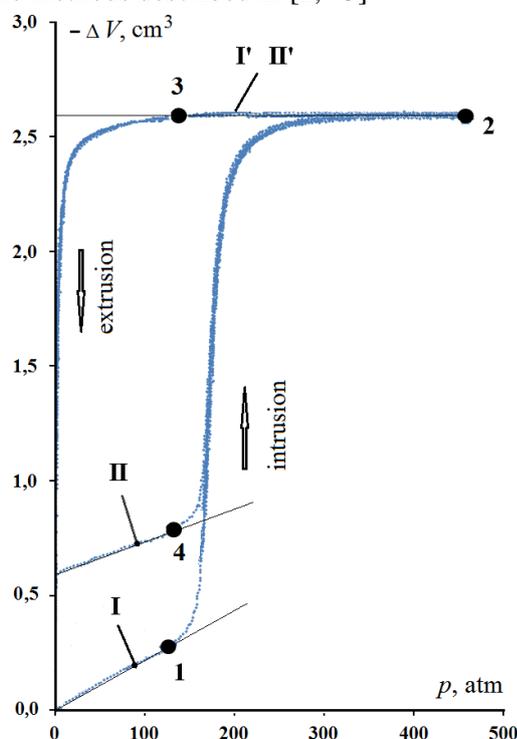


Figure 1. The dependence of the filled volume of the pressure when filling porous (I) and after spilling part of the liquid (II) when reducing excess pressure to zero within 15 seconds and after a timeout of 1 min according to the methods described in [2, 43]

The experiments showed that the volume fraction θ_2 of the liquid remaining in pores depends not only on the degree of preliminary filling θ_1 , but also on the escape expectation time t_{exp} . For this reason, to reduce errors and to improve the reproducibility of the measurements, the dependence of θ_2 on the expectation time t_{exp} was determined under the condition of the complete preliminary filling $\theta_1 = 1$. The experiments were performed as follows. The L23 porous medium was filled with water at an increase in the excess pressure to $p = 40$ MPa in time $t_{in} = 15$ s until complete filling. Then, excess pressure was reduced to zero in time $t_{out} = 15$ s. The times t_{in} and t_{out} were much larger than the

known characteristic filling–escape times for this system, which are < 0.1 s [42]. After that, the volume fraction θ_2 of the confined liquid was determined after the expectation time $t_{\text{exp}} = 60\text{--}10000$ s. On figure 1 shown the dependence of the filled volume of the pressure when filling porous (I) and after spilling part of the liquid (II) when reducing excess pressure to zero within 15 seconds and after a timeout of 1 min .To this end, we performed the aforementioned cycle of an increase and a subsequent decrease in the pressure. The dependence $\theta_2(t_{\text{exp}})$ for various temperatures is shown in Fig. 2 in a log–log scale.

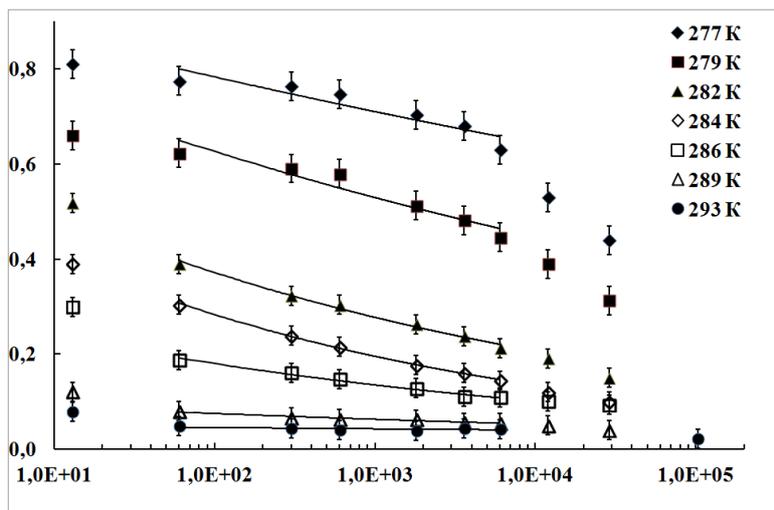


Figure 2. Dependences $\theta(t)$ at seven temperatures from 277 to 293 K in the time interval from 10 to $1 \cdot 10^5$ s. Experimental points in comparison with the power-law approximations $\theta \sim t^{-\alpha}$ shown by solid lines in the time interval from 60 to $6 \cdot 10^3$ s

It can be seen that the dependences of the volume fraction of the confined liquid on the time t_{exp} in this scale are straight lines within the measurement error. This indicates a power-law character of the relaxation of the volume fraction of the confined liquid θ_2 in the time t_{exp} . Correspondingly, the resulting dependences $\theta_2(t_{\text{exp}})$ were approximated by an inverse power law $\theta_2 = At^{-\alpha}$. According to Fig. 2, the slope α of the dependences $\theta_2 = At^{-\alpha}$ first increases with the temperature from $\alpha = 0.05$ to the maximum $\alpha = 0.16$ at $T = 283$ K and then decreases at $T > 283$ K to the value $\alpha = 0.04$ at $T = 293$ K (see Fig.). Such a dependence can be explained by the acceleration of the decay of the metastable state of the system at an increase in the temperature from $T = 277$ K to $T = 283$ K and by a transition at $T \geq 293$ K to a slower decay of the state of the confined liquid in which the volume fraction of the liquid θ_2 is independent of the temperature.

The experiments allow to recover the distribution function of the filled pore size for different relaxation times of the system obtained in the study of the temporal relaxation of metastable States of a nonwetting liquid in a porous medium. Figure 4 shows the recovered distribution function of the filled pore size for the system Liberar-23 – water at a temperature of 279K experiments and the waiting times 10 and 100 minutes, respectively.. Also in the figures for comparison, are the distribution function of the pores of the porous medium .

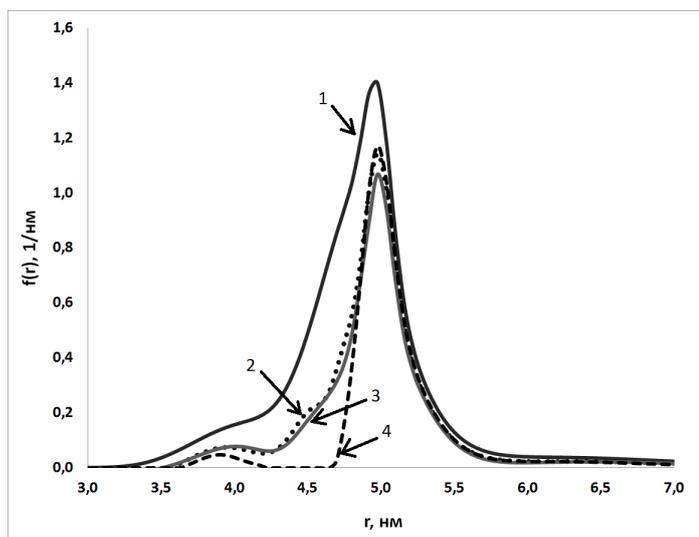


Figure 3. Distribution function of the liquid-filled pores corresponding to different relaxation times 1 - initial distribution, 2 - distribution of the pore with the remaining liquid after 1 minute 3 - the distribution of the pore with the remaining liquid after 10 minutes, 4 - the distribution of the pore with the remaining liquid after 100 minutes.

On fig. 3 presents the distribution function of the liquid-filled pores corresponding to different relaxation times 1 - initial distribution, 2 - distribution of the pore with the remaining liquid after 1 minute 3 - the distribution of the pore with the remaining liquid after 10 minutes, 4 - the distribution of the pore with the remaining liquid after 100 minutes. From figure 4 it is seen that in the relaxation process there is a change in the number of filled pores with sizes of 3.5-4.2 nm at maximum pore size distribution of 5 nm

Conclusion

From fig. 3 shows that relaxation process on the 0-100 times h occurs preferential leakage of fluid from local configurations of the pore sizes of 4.1-4.6 nm (figure 4.4) while discharge from the pores of the other radii in the distribution of the pore size occurs much more slowly (figure 4.2, 4.3). This confirms the idea of the existence in the studied disordered local environment configuration. While the system under consideration occurs, the range of times corresponding to the relaxation time of the cluster of filled pores of different radius. This means that not all of them, the liquid flows for the same time and the number of pores involved in the leakage, determined by the distribution function of the pore size depends on the time of observation. This looks disconcerting nature of the relaxation to a power law with $\alpha \sim 0.1$.

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