ORDER, DISORDER, AND PHASE TRANSITION IN CONDENSED SYSTEM

Anomalously Slow Relaxation of a Nonwetting Liquid in the Disordered Confinement of a Nanoporous Medium

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Abstract—The time evolution of the water–disordered nanoporous medium Libersorb 23 (L23) system has been studied after complete filling at elevated pressure followed by full release of overpressure. It is established that relaxation of the L23 rapidly flows out during the overpressure relief time, following the variation in pressure. At a temperature below that of the dispersion transition ($T < T_d = 284$ K), e.g., at $T = 277$ K, the degree of filling θ decreases from 1 to 0.8 within 10 s. The degree of filling varies with time according to the power law $\theta \sim t^{-\alpha}$ with the exponent $\alpha < 0.1$ over a period of $t \sim 10^5$ s. This process corresponds to slow relaxation of a metastable state of a nonwetting liquid in a porous medium. At times $t > 10^5$ s, the metastable state exhibits decay, manifested as the transition to a power dependence of $\theta(t)$ with a larger exponent. The relaxation of the metastable state of nonwetting liquid in a disordered porous medium is described in the mean field approximation as a continuous sequence of metastable states with a barrier decreasing upon a decrease in the degree of filling. Using this approach, it is possible to qualitatively explain the observed relaxation process and crossover transition to the stage described by $\theta(t)$ with a larger exponent.

1. INTRODUCTION

In recent years, much attention is devoted to researching the state and properties of disordered media such as glasses, colloids, polymers, loose materials, etc. [1−12]. Numerical simulations have been carried out [6, 7, 16, 18] and phenomenological models have been formulated, including dynamic heterogeneity (DH) [2, 5, 21], random first-order transition (RFOT) theory, topological bond-oriented local configurations [1, 6, 7, 16, 18, 27, 28], shear transformation zone (STZ) [1, 4, 9, 13, 19], etc. (see, e.g., [1−3, 10, 14, 20]), which employ the concept of local structures (configurations) that determine the properties of disordered media. These models have been used to describe the states and properties of glasses, colloids, polymers, and loose media, as well as liquid–glass transitions and sol–gel processes that lead to the appearance of random order. According to [1, 22, 23], these media are nonergodic and are characterized by anomalously slow relaxation of local nonequilibrium states, which is phenomenologically described by the law of stretched exponential relaxation [1, 8, 12, 27]. This anomalously slow relaxation implies that, for an arbitrarily long observation time (shorter than the lifetime of states), the system cannot reach any point in the phase space [1]. In phenomenological models of disordered media, the anomalously slow (power-law) relaxation is related to the assumption that metastable states of random local configurations form and decay in a disordered medium.

The class of disordered media includes, in particular, disordered porous media. Their structures can be studied by gas adsorption–desorption and mercury (liquid) porosimetry techniques. These methods provide information on the volume of pores, their surface area, and the pore size distribution function. Research into the states of a nonwetting liquid confined in a disordered structure of pores after removal of excess pressure opens new possibilities for studying the properties of disordered porous media [24−26].

In terms of statistical description, a system comprising a disordered nanoporous medium and an ensemble of a nonwetting liquid confined in the pores has certain specific features [25, 26]. The system has no dynamic degrees of freedom; hence, the dynamical heterogeneity as such cannot lead to the appearance and relaxation of local metastable configurations. The system can have a degenerate ground state characterized by the formation of a fractal percolation cluster of pores filled with a liquid. Only this ground state admits a hydrodynamic flow of the liquid filling the system and flowing out from filled pores, rather than capillary evaporation and condensation. Unlike the aforementioned phenomenological models, a statistical description of the confinement of liquid and dispersion transition [24−26] makes it possible to understand the physical origin of local structure formation,

calculate the potential barrier for the relaxation of metastable local configurations, consistently allow for their interaction, and describe the kinetics of anomalous relaxation of the system with these local structures [25, 26, 62].

The aim of this work was to study the phenomenon of anomalously slow relaxation of metastable states of a liquid confined in a disordered porous medium. The porous medium under consideration is a silica gel with disordered structures of the skeleton and pores formed during the sol–gel process. Relaxation of this system consists in anomalously slow extrusion of the confined nonwetting liquid from the porous medium. The relaxation of such states has not been studied before, although the fact of anomalously slow extrusion of a nonwetting liquid from porous media was sometimes pointed out (see, e.g., [29–32]). An approach to describing the anomalously slow relaxation of a confined nonwetting liquid is proposed that takes into account the appearance of local configurations of confined liquid clusters and considers their energies and interaction inside an infinite percolation cluster of filled pores. This approach makes it possible to qualitatively describe the observed power-law relaxation.

For many nonwetting liquids and disordered porous media, immediately after the removal of excess pressure, the porous medium immersed in a nonwetting liquid can be filled with this liquid only for an excess pressure above a certain critical value, which can be estimated using the Laplace formula. After subsequent removal of the excess pressure, this system can occur in an unstable state because surface forces will push the nonwetting liquid out. These phenomena are confirmed by numerous observations of hysteresis in the nonwetting liquid intrusion–extrusion curves for a porous medium immersed in this liquid [31, 33–43]. The characteristic extrusion time was determined in experiments with rapid compression of a porous medium immersed in a liquid and the subsequent fast removal of excess pressure [44]. For hydrophobized L23 silica gel (with a mean pore radius of $\bar{R} \sim 4$ nm and granule average size of 10 μm) filled with water, the complete liquid extrusion time was ~0.1 s. The fast extrusion mechanism was proposed in [44] using dynamic percolation theory [44, 45].

At the same time, it is known that many nonwetting liquids confined in disordered porous media are partly or completely retained in the pores even upon release of excess pressure. In these cases, only a fraction of the initially confined liquid can rapidly flow out from the medium. The confinement (nonextrusion) of nonwetting liquids was observed for water, aqueous solutions of salts and organic compounds, mercury and other liquid metals (e.g., Wood's alloy) in media such as hydrophobized silica gels (KSK-G, PEP 100, PEP 300, Fluka 60, Fluka 100, and C8W (Waters)) and porous glasses (Vycor, CPG) [31–43, 48, 49]. These media differ in the degree of hydrophobicity, porosity,

average pore size (0.5–20 nm) and average granule size (10–100 μm), and the width of the pore size distribution. It should be noted that the confinement effect is not related to a change in the phase state of the liquid. Indeed, according to [29, 50], the properties of a confined liquid in a medium with the pore radius $R > 1$ nm at $T > 273$ K do not differ from properties of the bulk liquid. The confined liquid can be retained in a porous medium for several hours, days, and even months. For example, in the mercury–porous glass system [29], the weight of porous glass samples with confined mercury and the results of neutron scattering experiments did not change for several months. In some other systems consisting of mercury and porous glasses (Vycor, CPG) and silica gels, it was found that the volume of the confined liquid depends on the extrusion observation time and the granule size of the porous medium [46, 51].

Studies showed that volume fraction θ of the confined liquid can vary from several to a hundred percent [31–33, 43, 46, 49, 52, 53]. In particular, for L23 silica gel–water system at $T = 279$ K, confinement of about 100% of the liquid changes to a small (~5%) volume fraction of retained liquid for a variation in temperature of $\Delta T \approx 10$ K. If the degree of filling θ of pores with the confined liquid is above the threshold θ_c of percolation through filled pores ($\theta_c = 0.15$–0.35, depending on the model of the porous medium [54]), the porous medium can retain the confined liquid for an observation time of 10–10^5 s despite the fact that the liquid can flow out through filled pores (which form an infinite percolation cluster at $\theta > \theta_c$). In other cases, when $\theta < \theta_c$, only individual clusters of filled pores are formed in the porous medium. Analogous states have been observed in the water–Fluka 100 C18 system [47], since there are no pathways for liquid extrusion from these clusters via filled pores. A possible mechanism of liquid discharge from clusters of filled pores can be related to recondensation, that is, capillary evaporation followed by capillary condensation at the porous medium–surrounding liquid interface [55, 56]. This work is devoted to studying the process of confined liquid extrusion from pores at $\theta > \theta_c$.

Previously [31, 32], it was established for water and L23 or Fluka 100 C18 porous media systems that the volume of the confined liquid critically depends on both the initial degree of filling and the temperature (dispersion transition). This behavior cannot be explained by notions of liquid intrusion–extrusion in the system of individual pores based on the Laplace relation with a phenomenological contact angle [46]. These critical dependences imply that the confinement of a fraction of the nonwetting liquid can be attributed to the collective interaction between liquid clusters in neighboring pores depending on the degree of filling. Correlation effects of the interaction between liquid clusters in confinement were considered in [57–59]. The state and relaxation of an ensem-
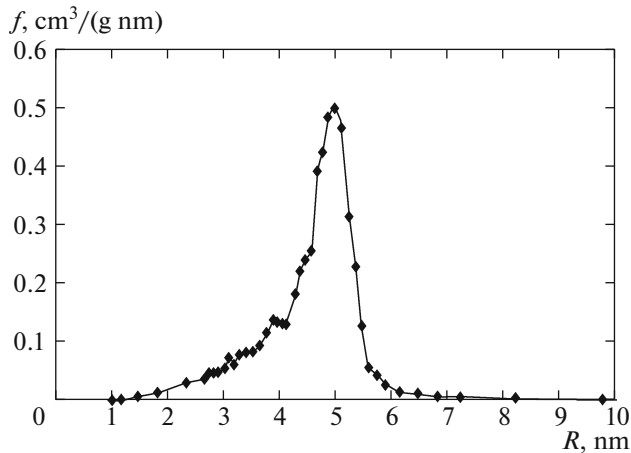
Fig. 1. Pore size distribution function for Libersorb 23 porous medium according to BJH method.

ble of liquid clusters in pores was described using the lattice gas model [58, 59], according to which transport proceeds by vapor diffusion from a filled pore to a neighboring empty pore [60, 61].

Confinement of a nonwetting liquid in a disordered porous structure and the dispersion transition kinetics in this system were recently described [62] using analytic percolation theory and statistical fluctuation theory. Within this approach, the extrusion of the liquid and its confinement were considered for the ground state of the disordered porous medium, which is characterized by the formation of an infinite fractal percolation cluster of filled pores. The energy barrier of a metastable state is determined as the difference between the surface energy of the interaction of a liquid cluster in a pore with the skeleton of the medium (which pushes the nonwetting liquid out) and the surface energy of "multiparticle interaction" between the liquid cluster in a pore and liquid clusters in neighboring pores. This energy barrier forms a random potential relief in the space of the porous medium on the shell and in the volume of a percolation cluster of filled pores. According to [62], the liquid extrusion reduces to overcoming numerous peaks of this potential relief. Description of the relaxation of a metastable state of the confined liquid, which has been proposed in [62] based on calculations of the distribution of filled pores with respect to liquid extrusion times, is also used in this work for a porous medium with narrow distribution of pore sizes ($\Delta R/R \ll 1$).

In Section 2, we describe a method of step-by-step determination of θ for a period up to 10^5 s. Using this method, it is possible to reproduce and monitor the initial state of the confined liquid over a period of $t > 10$ s, which is greater than the time of spontaneous barrierless extrusion of this liquid at $\theta > \theta_c$.

This study revealed an anomalously slow extrusion of a confined liquid under conditions of initial degree

of filling θ of pores both above and below the percolation threshold (Section 2.2). Experimental data for $\theta > \theta_c$ are described by an inverse power dependence as $\theta \sim t^{-\alpha}$ with exponents within $0 < \alpha < 0.1$.

Theoretical analysis of the results was aimed at describing the general pattern of appearance and relaxation of metastable states of a nonwetting liquid in a disordered porous medium in the mean-field approximation (Section 3).

2. EXPERIMENTAL

2.1. Porous Medium

The experiments were performed with a Libersorb 23 (L23) nanoporous medium based on KSK-G silica gel, in which a disordered structure of pores is formed using the sol−gel process. The surfaces of pores of KSK-G silica gel were modified by alkylsilanes at the laboratory headed by Prof. G.V. Lisichkin (Moscow State University) in order to impart hydrophobic properties to it [63, 64]. The characteristics of samples of L23 porous medium were determined by the adsorption of nitrogen in an Autosorb IQ (Quantachrome, United States) analyzer for studying low-temperature sorption and a Micro-Ultrapyc 1200e helium pycnometer. The density of the porous medium was $\rho = 1.7798 \pm 0.0016$ g/cm^3, the specific volume of pores was $V_p = 0.62 \pm 0.02$ cm^3/g, the porosity of the material was $\varphi = 0.52$, the specific surface was $S_p = 199 \pm 7$ m^2/g, and the mean size of granules in the L23 powder was ~10 μm.

Figure 1 shows the pore volume distribution function. This curve qualitatively characterizes the pore size distribution with respect to their radii. The mean radius of pores is $\langle R \rangle = 5.0 \pm 0.2$ nm. The full width at half maximum (FWHM) of this distribution is $\Delta R = 0.4 \pm 0.1$ nm, and $\Delta R/\langle R \rangle \leqslant 0.1$. The distribution tails are observed in regions of large and small pore sizes.

2.2. Measurement Techniques

The aim of our experiments was to determine the time variation of the volume fraction θ of pores filled with a confined liquid. The confined liquid is defined as the fraction of liquid retained in pores after their complete filling at increased pressure and the subsequent release of excess pressure. The other fraction of liquid rapidly flows out of the pores during the pressure release time. The extrusion time of the latter fraction from the L23−water system can be smaller than 1 s [47]. In this work, we studied the time dependence of volume fraction θ of pores with retained liquid in a slow liquid extrusion process, i.e., the relaxation of the state of liquid confined in the porous medium. The scale of the characteristic liquid extrusion times can vary depending on the mechanism of liquid transport through the system of filled pores and/or the mechanism involving capillary evaporation and subsequent
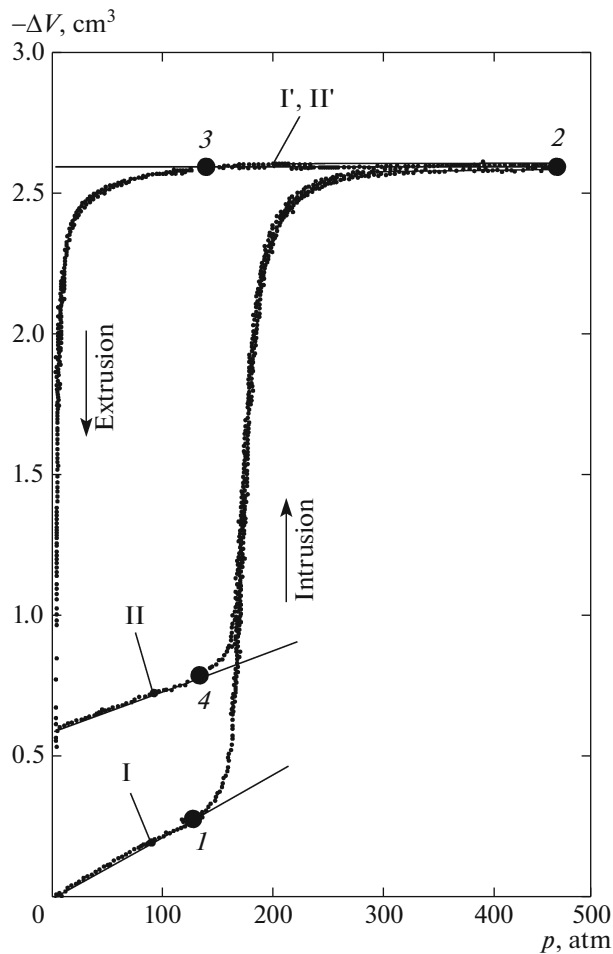
Fig. 2. Pressure dependences of changes in volume of L23−water system at $T = 286$ K for two successive intrusion−extrusion cycles.

capillary condensation at the interface between the bulk liquid and a granule of the powder of the porous medium immersed in this liquid. The latter mechanism can obviously be effective in case of the formation of an "infinite" percolation cluster of empty pores, i.e., when the degree of pore filling with the confined liquid is $\theta < \theta_{c1} = 0.7−0.85$.

The method used to measure the volume of the nonwetting liquid−porous medium system was similar to the mercury [65] or water [63] porosimetry technique, according to which a preliminarily dried and degassed sample of L23 porous medium with a mass of up to 6 g in a water-permeable container was placed in a high-pressure chamber. The remaining free volume of the chamber (28 cm^3) was completely filled with distiller water. A rod was introduced into the chamber through seals. The chamber was equipped with a thermostat system, which allowed experiments to be performed at controlled temperatures from 243 to 393 K. Prior to measurements, the assembled chamber was kept at a given temperature for no less than 1 h. The

temperature during measurements was maintained accurate to within ±0.2 K. The chamber was mounted in a setup described in [31], which ensured programmed loading of the rod introduced into the chamber, measurement of the force, and displacement of the rod. Pores in the sample were filled under a pressure produced by compression of the system in a closed volume as the rod was introduced into the chamber. Seals ensured the impermeability of the chamber filled with water and porous medium. The force (F) acting on the rod was measured using a CWH-T2 strain gauge (Dacell, South Korea); displacements (l) of the rod were measured by a Model 8719 potentiometric displacement sensor (Burster, Germany). The pressure (p) in the chamber was determined as $p = F/S_r$, where $S_r = 0.785$ cm^2 is the area of the cross section of the rod. A change in the internal volume of the chamber (V) was determined as $V = lS_r$. Sensors data were recorded at a frequency of 1 kHz.

An increase in the pressure inside the chamber resulted in elastic straining of the chamber, liquid, and porous medium. The filling of pores in L23 porous medium with water was observed only at pressures above 120×10^5 Pa. This made it possible to determine the effective compressibility of the chamber, as well as the compressibilities of water and porous medium in additional experiments at pressures below 120×10^5 Pa (see Fig. 2); the corresponding data were taken into account in determining the volume of filled pores at a given pressure. In these experiments, we used a step-by-step procedure to determine the degree of filling (θ) of pores in the medium with confined liquid as a function of time (t). The θ value was determined for every observation time (t_i) of the liquid outflow by extrusion and/or evaporation. Then, the porous medium−liquid system was returned to the initial state and $\theta(t_j)$ value was determined for different times t_j both larger and smaller than t_j. The $\theta(t)$ function was determined by multiple repetition of this procedure for various t_i. Every step of the procedure consisted of two successive intrusion−extrusion cycles performed for a given t_i.

Figure 2 shows the typical pressure dependences of volume change in the L23−water system at $T = 286$ K for two successive cycles at the first step of the measurement procedure. The curves in Fig. 2 for the preliminarily dried and degassed porous medium are plotted for subtraction of changes in the system volume related to the compressibility of the liquid, the skeleton of the porous medium, and the chamber. Curve I corresponds to a decrease in the volume of the empty porous medium caused by an increase in pressure during the first cycle. Curve I' shows an increase in the volume with decreasing pressure. Three regions in the $V(p)$ curve can be distinguished at the stage of increasing pressure. Region 0−1 corresponds to compression of the empty porous medium, the slope of this linear segment being determined by the compressibility of the empty porous medium. It should be noted
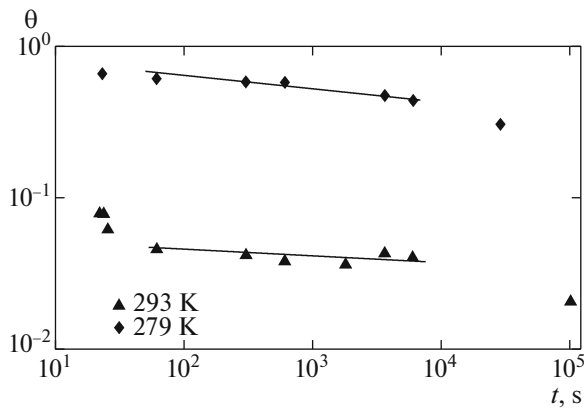
Fig. 3. Plots of θ vs. relaxation observation time t at temperatures $T = 279$ and 289 K.

that the filling of pores in granules of the porous medium immersed in liquid in the chamber was observed neither at the initial state at zero excess atmospheric pressure $\Delta p = p - p_{atm} = (0.05 \pm 0.05) \times 10^5$ Pa (when empty pores may contain saturated water vapor) nor at high pressures up to 120×10^5 Pa at point *1* in segment 0−1 (when the observation time is smaller than 15 h). Region 1−2 of curve I corresponds to the filling of accessible pores in the empty porous medium. At a pressure of $p = 450 \times 10^5$ Pa, about 99.8% pores are filled. The volume of all filled pores in the sample is equal to the difference $|V_2 - V_1|$. When the pressure decreases below point *3* on curve I', volume V exhibits a decrease that corresponds to the extrusion of liquid from pores, which is described by curve I'. The main decrease in the volume V is observed at low pressures comparable with the error of pressure measurements, so that the volume of the confined liquid can be determined from the intersection of $V(p)$ curve and the *y* axis only to within $\delta V/V \sim 1$. For this reason, the volume of pores in these experiments was determined in two successive intrusion–extrusion cycles.

Prior to repeated filling of the system in the second cycle, some pores contain a residual confined liquid and, when the pressure in the second cycle increases above point *4* in curve II, only a fraction of empty pores are filled. The volume of these empty pores is $|V_2 - V_4|$, and the difference between the volumes of filled pores in the first and second cycles determines the volume of pores filled with the liquid retained after the first cycle, $V_t = |V_2 - V_1| - |V_2 - V_4|$, so that $\theta(t) = V_t/|V_2 - V_1|$. The relative compressibilities in the regions corresponding to filling of the empty and partially filled porous medium are almost the same within the measurement error, $(7.5 \pm 0.9) \times 10^{-9}$ Pa^{-1}. After complete filling, the system forgets the prehistory of the formation and relaxation of the preceding initial state, so that a new initial state of the confined liquid is formed upon its partial extrusion (curve II'). In this

way, the total volume $\theta(t)$ of all empty pores at any step in the first filling cycle can be determined. The volume of pores that remain empty after the extrusion of liquid in the time interval from the onset of extrusion in the first cycle (point *3*) to the beginning of filling due to increase in the pressure (point *4*) in the second cycle is determined upon the repeated filling.

Therefore, volume V according to this method is determined for time t that has passed from the onset of liquid extrusion in the first cycle (point *3*). This period of time includes interval t_1 required to reach a "zero" excess pressure $\Delta p = p - p_{atm} = (0.05 \pm 0.05) \times 10^5$ Pa and interval t_i to the onset of repeated intrusion at point *4* in the second cycle.

Since the time of pressure release ($t_1 = 10$ s) in the first cycle is much greater than the time of hydrodynamic extrusion of a fraction of the liquid at $\theta > \theta_c$, a decrease in the volume adiabatically follows the decrease in the pressure. Thus, the initial state of the system is formed for a time that is fixed in all measurements ($t_1 = 10$ s), and relaxation of the metastable state of the confined liquid begins at $t > t_1$. The volume V_t of confined liquid in the metastable state in these experiments refers to the observation time of relaxation (extrusion of the liquid) $t = t_i$.

In order to check the reproducibility of the initial state, we performed additional experiments with multiply repeated measurements of $\theta(t)$ at a fixed time of $t = t_1 + t_i = 1$ min. It was established that the spread of θ values measured at $t = 1$ min is smaller than the measurement error. An additional series of measurements showed that $\theta(t_i)$ and the value measured at some different time t_j are independent of the order of these measurements. Multiple intrusion–extrusion–confinement experiments with the nonwetting liquid at temperatures within $T = 277-293$ K with the subsequent removal of confined water from the L23 porous medium by evacuation drying at $T = 343$ K, performed before and after measuring $\theta(t)$, confirmed that the properties of the porous medium did not change. The specific volume of pores, pressure p_{in} of the intrusion onset at point *1* (Fig. 2), and pressure p_{out} of the beginning of liquid outflow (extrusion) at point *3* remained unchanged within the measurement error after more than 100 identical cycles.

2.3. Experimental Results

Figure 3 shows the values of the degree of filling θ of pores with the confined liquid measured for various relaxation observation times t at temperatures $T = 279$ and 293 K. Experimental points in Fig. 3 represent the averaged results of up to six measurements at each time t. The spread of θ values does not exceed the measurement error. This confirms the reproducibility of the initial state of the liquid–disordered porous medium system after "memory loss" of the preceding states

Confidence of power-law approximation $\theta \sim t^{-\alpha}$ of experimental θ values in Figs. 4 and 5

T, K	277	279	282	284	286	289	293
R^2	0.8776	0.9003	0.9625	0.9985	0.9814	0.9426	0.3150

upon complete filling in the first and second intrusion–extrusion cycles.

Between temperatures $T = 293$ and 279 K, the water–L23 porous medium system undergoes a dispersion transition for which liquid dispersed in the porous medium pass to a metastable state with decreasing temperature [24]. With an increase in temperature, an adiabatic transition from almost total nonextrusion of the liquid at $T = 279$ K to its almost total extrusion at $T = 293$ K takes place in a narrow ($\Delta T \approx 10$ K) temperature interval near the critical temperature. At $T = 277$ K and relaxation observation times from 13 to 3×10^5 s, the degree of filling decreases from 0.8 to 0.6 (see Fig. 4). In this case, $\theta > \theta_c$ (where $\theta_c = 0.15$–0.3 is the percolation threshold) and relaxation proceeds under conditions of the formation of an "infinite" percolation cluster of filled pores. Therefore, the liquid can leave the porous medium via the mechanism of extrusion through filled pores of the percolation cluster. At $T = 293$ K and times t in the interval from 13 to 10^5 s, the degree of filling θ varies from 0.08 to 0.02. At these degrees of filling below the percolation threshold, the confined liquid occurs in separate pores surrounded by empty pores. For this reason, the volume of the confined liquid can decrease by the well-known gas-phase transport mechanism, which involves capillary evaporation from the liquid surface in filled pores, diffusion of vapor in the residual gas of the infinite percolation cluster of empty pores, and capillary condensation at the interface between granules of the porous medium and the bulk liquid [58, 59].

According to Figs. 3–5, θ exhibits slow relaxation within the time interval 60 s $< t < 6 \times 10^3$ s at $T = 279$ K, and the log–log plot of $\theta(t)$ is described by a straight line within the measurement error. An analogous picture is observed at $T = 293$ K for a different (gas-phase) transport mechanism in the time interval 60 s $< t < 6 \times 10^3$ s. However, the slope of $\theta(t)$ plot at the higher temperature is smaller and, therefore, the relaxation rate is lower in accordance with a slower gas transport at $T = 293$ K.

Figures 4 and 5 show the time dependences $\theta(t)$ measured for seven temperatures from 277 to 293 K in the time interval from 60 to 6×10^3 s. As can be seen, the experimental data can be described within the measurement error by the power function as $\theta \sim t^{-\alpha}$ with a temperature-dependent exponent α. Figure 5 shows that the slope of the linear log–log plot of $\theta(t)$ increases with temperature from 277 to 286 K and then decreases when the temperature increases further up to 293 K. Therefore, exponent α has an extremum at $T \approx 285$ K that corresponds to the maximum extrusion rate of the confined liquid at this temperature.

Figure 6 shows the temperature dependence of exponent α for the power-law approximation $\theta \sim t^{-\alpha}$. The corresponding confidence parameter R^2 (see table) of experimental data in Figs. 4 and 5 was used to estimate the uncertainty of the α values. The small confidence parameter ($R^2 = 0.315$) of the power approximation at $T = 293$ K may be related to a change in the relaxation mechanism. In the case under consideration, relaxation at $\theta < \theta_c$ is based on the well-known vapor transport mechanism [58, 59]. Accord-
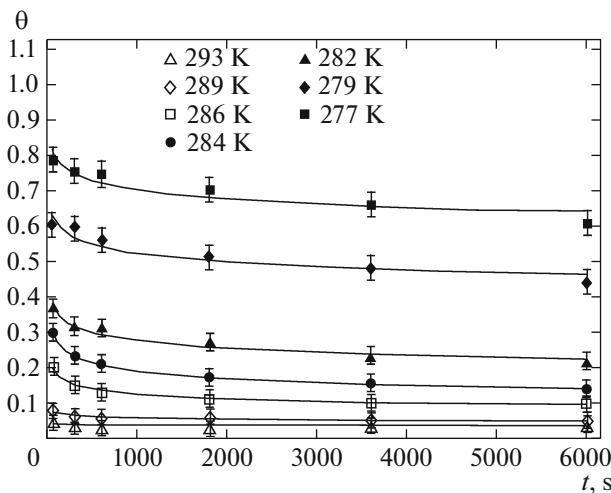

Fig. 4. Time variation of $\theta(t)$ at seven temperatures from 277 to 293 K in time interval from 60 to 6×10^3 s. Points represent experimental data; solid lines, approximation by power function $\theta \sim t^{-\alpha}$.
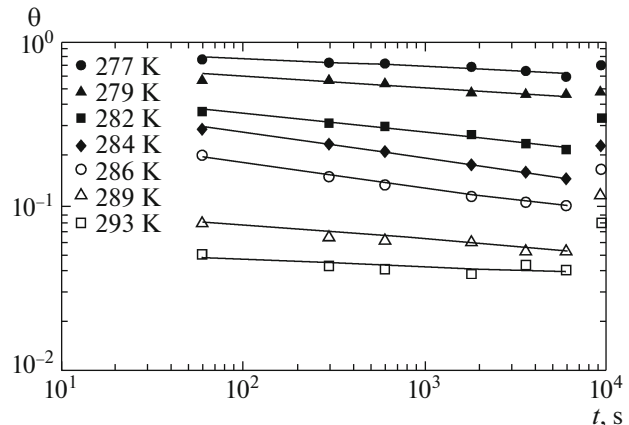

Fig. 5. Double logarithmic plots of $\theta(t)$ measured at seven temperatures from 277 to 293 K in time interval from 60 to 6×10^3 s. Points represent experimental data; solid lines, approximation by power function $\theta \sim t^{-\alpha}$.
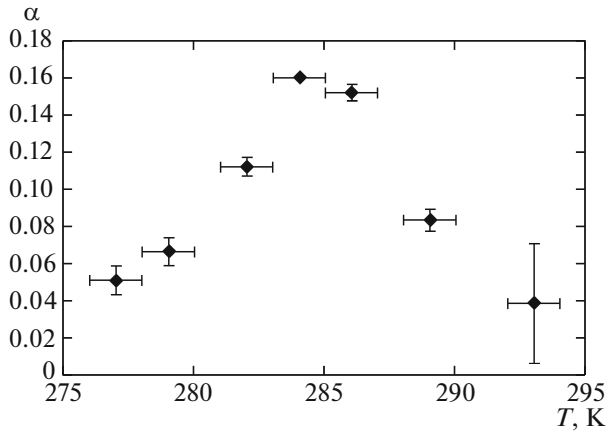
Fig. 6. Plot of exponent α vs. temperature. Uncertainty of ordinate determined as $\alpha(T)(1 - R^2(T))$.

ing to this mechanism, the hydrodynamic flow time in a channel for a Knudsen gas is independent of the channel radius and the relaxation should obey a logarithmic rather than a power law, because the Knudsen number in experiments at $p = 1 \times 10^5$ Pa, $\bar{R} = 4$ nm, and $T \approx 300$ K is Kn > 10.

The obtained experimental data lead to the following conclusions. When the excess pressure is varied from 450×10^5 to about 120×10^5 Pa, the extrusion of liquid from the filled porous medium is not observed in the entire temperature range under study. The extrusion begins at an excess pressure of $p < 120 \times 10^5$ Pa. At temperatures $T > 286$ K, the pressure release from 120×10^5 Pa to zero for $\tau_p = 10$ s is accompanied by a decrease in the degree of filling below the percolation threshold θ_c via filled pores. In the time interval from 10 to 10^6 s, the degree of filling θ varies from 0.08 to 0.02 according to the power law $\theta \sim t^{-\alpha}$ with an exponent of $\alpha \leqslant 0.05$.

At $T < 282$ K, the pressure release from 120×10^5 Pa to zero for $\tau_p = 10$ s is accompanied by a partial outflow of about 60% of confined liquid. The degree of filling remains above the percolation threshold θ_c and the possibility of rapid (within $\tau_0 \sim 0.1$ s) [44] hydrodynamic extrusion of liquid via a percolation cluster of filled pores is retained. However, this does not take place, and the degree of filling decreases between $t = 10$ s and 6×10^3 s according to the power law $\theta \sim t^{-\alpha}$ with an exponent of $\alpha \leqslant 0.2$.

3. RELAXATION SCENARIO

The results of experiments showed that two different relaxation scenarios were possible after filling of the porous medium and the subsequent release of excess pressure. At temperatures $T > 284$ K, most of the confined liquid (>70%) occurs in an unstable state and flows out of the porous medium within the char-

acteristic time of the release of excess pressure ($t \sim 10$ s). The remaining part of the liquid confined in a fraction of filled pores below the percolation threshold $\theta < \theta_c$ slowly relaxes at times $t \gg 10$ s according to the power law $\theta \sim t^{-\alpha}$ with a small exponent ($\alpha \leqslant 0.05$). At temperatures $T < 284$ K, a fraction of the liquid after intrusion at excess pressure and release of excess pressure occurs in an unstable state and flows out within the time of pressure release ($t = 10$ s) through filled pores of the infinite percolation cluster. Partial extrusion of up to 60% of the liquid can take place within this time at $T = 282$ K. According to [62], the remaining large (above 40%) part of the liquid occurs in a metastable state and flows out slowly. For observation times $t < 6 \times 10^3$ s, the degree of filling decreases according to the power law $\alpha \sim t^{-\alpha}$ with a temperature-dependent exponent of $\alpha \leqslant 0.2$. For $t > 6 \times 10^3$ s, the metastable state exhibits decay.

3.1. Formation of a Metastable State

Let us consider the dynamics of extrusion of the nonwetting liquid from the nanoporous medium. The porous medium contains pores of various dimensions, consists of granules with sizes much greater than the maximum pore diameter, and admits the formation of an infinite percolation cluster of pores. Therefore, the porous medium can be considered infinite.

The characteristic time of release of excess pressure in our experiments was $\tau_p \sim 10$ s, and hence, $\tau_p \gg \tau_0$ ($\tau_0 \sim 0.1$ s) [44]. For $\tau_p \gg \tau_0$, the process of liquid extrusion can be considered as taking place in a quasi-stationary medium at a slowly varying excess pressure $p(t)$ that decays to zero, so that $\Delta p = p - p_{atm} = (0.05 \pm 0.05) \times 10^5$ Pa. Under these conditions, extrusion of the nonwetting liquid from the porous medium filled with this liquid at pressure p requires performing a work for emptying pores. A filled pore in the medium can occur in various states corresponding to different extrusion times (depending on the pore radius) [62]. The time of liquid extrusion from a pore can be calculated using statistical fluctuation theory. Let us consider a change in the state of the liquid–porous medium system upon extrusion of the liquid from a pore surrounded by empty and filled pores (in a partly filled porous medium). Surrounding pores are connected to the pore under consideration via channels ("throats") with mouths in which menisci are formed provided that one of the two connected pores is not filled with the liquid.

According to [66], the probability w of the system changing state per unit time due to liquid extrusion from the studied pore under the action of fluctuations obeys the following relation:

$$w \sim \exp(\Delta S),$$

where ΔS is the change in the entropy of the system upon extrusion of liquid from the pore. The proportion-

ality coefficient in this relation is determined by the extrusion dynamics of the liquid. Let us assume that the change in system temperature during this process can be ignored. This assumption corresponds to the small thermal effect observed in experiments [39, 67]. In this case, probability w can be written as follows:

$$w = w_0 \exp(-\delta A/T), \tag{1}$$

where w_0 is the pre-exponential factor that takes into account the dynamics of liquid extrusion from the porous medium and δA is the isothemal work that must be done for the extrusion of liquid from the pore.

Equation (1) suggests that the time of liquid extrusion from the pore can be expressed as

$$\tau = \tau_0 \exp(\delta A/T). \tag{2}$$

where $\tau_0(R)$ is the hydrodynamic time of extrusion determined by the liquid outflow dynamics from the porous medium. This time can be estimated as follows. If the liquid flows out from a pore of radius R through a channel of filled pores with the same radius, then $\tau_0 = 4\pi R^3/3Q(R)$ [62]. In this case, we have $Q(R) \sim R^4$ [68] and, hence,

$$\tau_0 \sim 1/R. \tag{3}$$

The expression for δA in the case of a spherical pore with radius R can be written as follows [62]:

$$\delta A(R, \theta) = pV + \delta\varepsilon,$$
$$\delta\varepsilon = \delta\varepsilon_1(R) + \delta\varepsilon_{int}(R, \theta),$$
$$\delta\varepsilon_1(R) = -\delta\sigma(1 - \eta(R)), \quad \eta(R) = \frac{\langle S_m(T) \rangle}{S}, \tag{4}$$
$$\delta\varepsilon_{int}(R, \theta) = \sigma W(z, \theta)\eta(R),$$

where $V = 4\pi R^3/3$ and $S = 4\pi R^2$ are the volume and surface area of the pore, respectively; $\langle S_m \rangle$ is the mean area of menisci in the local configuration; $\delta\sigma$ is the change in the specific energy of the solid surface (skeleton of the porous medium) upon extrusion of the liquid; and σ is the specific energy of the nonwetting liquid−gas interface.

It follows from Eqs. (4) that $\delta\varepsilon_1$ depends on the change in the surface energy upon extrusion of liquid from the pore and therefore takes into account the interaction of the liquid with the skeleton of the porous medium. The value of ε_{int} is determined as the mean change in surface energy of menisci in the mouths of pores surrounding the pore out of which the liquid flows. Therefore, $\delta\varepsilon_{int}(R, \theta)$ can be treated as describing the effective "multiparticle interaction" of a liquid cluster in the pore with neighboring pores.

The function $\eta(R)$ in Eqs. (4), which is defined as the ratio of the mean area of menisci to the pore area, was calculated previously [69] for a medium containing pores with various radii taking into account correlations in the spatial arrangement of pores in the medium: $\eta \sim q(R_0/R)^{-\gamma}$, where $\gamma \approx 0.3$, $q \sim 1$ and R_0 is the minimum radius of pores determined by the pore

radius distribution function. In order of magnitude, R_0 is the mean pore radius divided by the average number of nearest neighbors, $R_0 \sim \overline{R}/\overline{z}$.

The function $W(z, \theta)$ in Eqs. (4) is defined as the average difference between the numbers of menisci after and before emptying of the pore and can be expressed as

$$W(z, \theta) = \sum_{n=0}^{z-1} (1 - \theta)^n (P(\theta))^{z-n} \frac{z - 2n}{z} \frac{z!}{n!(z-n)!}, \tag{5}$$

where $P(\theta)$ is the probability that the filled pore belongs to the infinite cluster of filled pores. In this expression, the first and second factors correspond to the probability that the filled pore is surrounded by n empty and $z - n$ filled pores, respectively, while the third factor determines the difference between the relative numbers of menisci after ($z - n$) and before (n) filling of the pore. The combinatory factor takes into account variants of the arrangement of n menisci over the nearest neighbors of the given pore and corresponds to degeneracy of the local geometric state of the "pore and neighboring filled pores" configuration in the first coordination sphere. Thus, each term in sum (5) describes a change in the number of menisci at a fixed relation between the numbers of filled and empty pores. The summation in Eq. (5) involves all possible variants of the mutual arrangement of empty and filled pores and makes it possible on the average to take into account variation of the local configurations "pore and its environment of filled and empty pores" in the disordered porous medium. The number z of nearest neighbors is related to the porosity φ and can be calculated for various models of the porous medium [70]. In particular, for a model of randomly distributed spheres, $z = -8\ln(1 - \varphi)$, where φ is the porosity of the medium [70]. An analysis of Eq. (5) shows that function $W(z, \theta)$ weakly depends on a particular choice of the probability $P(\theta)$ that a filled pore belongs to the infinite cluster of filled pores [62].

Equations (4) and (5) determine the energy of the barrier of a metastable state of the confined liquid, which is calculated in the mean field approximation by averaging over the number of empty neighbors of the pore under consideration and over the radii of neighboring pores. In these calculations, the contribution from configurations with pores of various sizes was ignored in view of the assumption of a narrow distribution of pore sizes, $\Delta R/\overline{R} \ll 1$. It follows from Eqs. (4) that potential barrier dA is determined by the pressure p and the surface energy $\delta\varepsilon$ of liquid in the pore during extrusion and depends significantly on the pore radius R. The product pV is always positive, whereas the surface energy $\delta\varepsilon$ has a maximum ε_{max} at the pore radius $R = R_{max}(z, \theta)$ and can change sign at radii $R^*(z, \theta)$ for which $\delta\varepsilon_{int}(R, \theta) = |\delta\varepsilon_1|$. This condition yields the following expression:
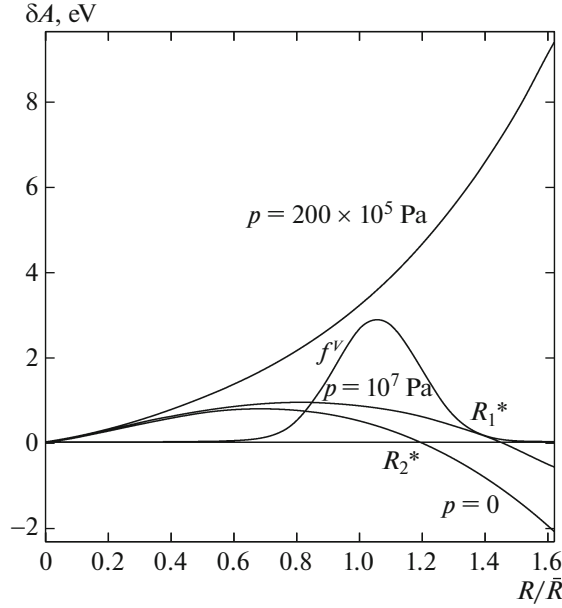
Fig. 7. Potential barrier δA vs. pore radius R in case of complete filling ($\theta_1 = 1$) of medium at $T = 277$ K and various pressures; $\bar{R} = 5$ nm; pore volume distribution function $f^V(R)$ with $\Delta R / \bar{R} = 0.1$; $z = 6$; R_1^* and R_2^* are radii above which $\delta A < 0$ at excess pressures $p = 10^7$ Pa and $p = 0$, respectively.

$$R^*(z, \theta) = q^{1/\beta} R_0 \left(1 + \frac{\sigma}{\delta\sigma} W(z, \theta)\right)^{1/\beta}, \qquad (6)$$

where $R_0 \sim \bar{R}/\bar{z}$ is the minimum size of pores in the pore volume distribution $f^V(R)$. According to Eqs. (4) and (6), the surface energy of pores with radii $R < R^*(z, \theta)$ is positive ($\delta\varepsilon > 0$). In this case, the potential barrier δA is positive at any pressure p. According to Eq. (2), this implies that the time of extrusion from such a state, $\tau = \tau_0 \exp(\delta A / T)$, is exponentially large as compared to the hydrodynamic time ($\tau \gg \tau_0$).

In pores with $R > R^*(z, \theta)$, the surface energy is negative. In this case, Eq. (4) shows that the barrier δA in this case depends critically on the pressure. Indeed, the barrier is positive at pressures $p > p_c = \delta\varepsilon/V$ and negative at $p < p_c = \delta\varepsilon/V$. The critical pressure depends on the pore radius: $p_c = p_c(R)$. In a porous medium under excess pressure p, the barrier for some pores is negative and, according to Eq. (2), the liquid can flow out from these pores within hydrodynamic time $\tau_0 \sim 0.1$ s. For another fraction of pores, the barrier is positive and, according to Eq. (2), the time of liquid extrusion from these pores is exponentially large compared to the hydrodynamic time: $\tau = \tau_0 \exp(\delta A / T) \gg \tau_0$.

It follows from Eq. (6) that the quantities $R^*(z, \theta)$, and $\varepsilon_{max}(z, \theta)$ depend on the temperature because the surface tension coefficients $\sigma(T)$ and $\delta\sigma(T)$ are temperature dependent. An analysis shows that both

$R^*(z, \theta)$, and $\varepsilon_{max}(z, \theta)$ grow with decreasing temperature and increasing degree of filling [25]. Correspondingly, the potential barrier δA also depends on the temperature, increasing with a decrease in the temperature and an increase in the degree of filling.

Figure 7 shows the dependence of potential barrier δA on the pore radius in case of complete filling ($\theta_1 = 1$) at $T = 279$ K and various pressures, as calculated by Eqs. (4) and (5) using data [57] for the surface tension and its temperature dependence $\sigma(T)$. The surface tension of water at $T = 293$ K is 75 mJ/m^2 [57]. The value of $\delta\sigma$ and its temperature dependence for the system under consideration were determined from the temperature dependence of the extrusion pressure by the method described in [57]. The $\delta\sigma$ value at $T = 293$ K is 22 mJ/m^2. The value of $R_0 \sim \bar{R}/\bar{z}$ was estimated in the framework of the model of randomly distributed spheres (RDS) [24, 25], which yielded $R_0 \sim 1$ nm for a porosity of $\varphi \sim 0.5$ and a mean pore radius of $\bar{R} \sim 5$ nm.

As can be seen from Fig. 7, the energy barrier for liquid extrusion at $p > 200 \times 10^5$ Pa is $\delta A \sim 4$ eV. A decrease in the pressure to $p \sim 10^7$ Pa leads to a change in the barrier height. For the pores with radii $R > R_1^*$, the potential barrier for liquid extrusion vanishes, since $\delta A(R > R_1^*) \leqslant 0$ (Fig. 7). For pores with $R < R_1^*$, the barrier $\delta A(R < R_1^*)$ is positive and increases with decreasing R within the pore volume distribution $f^V(R)$.

The time variation of the volume fraction of liquid retained in the porous medium during the pressure release for $t < \tau_p \sim 10$ s can be calculated by taking into account that the extrusion at $\tau_p \gg \tau_0$ can be treated as a quasi-static process at slowly decaying external excess pressure $p(t)$. Then, following [44], the probability of finding a pore in the filled state at pressure $p(t)$ can be determined as

$$w_0(p(t), R) = \left[1 + \exp\left(-\frac{\delta A(p(t), \theta, R)}{T}\right)\right]^{-1}. \qquad (7)$$

Here, the value of δA (that plays the role of a potential barrier for extrusion) is defined by Eq. (4). In this case, time variation of the volume fraction of liquid retained in the porous medium during pressure release at $t < \tau_p$ can be determined by solving the self-consistent equation

$$\theta(t) = \int_0^\infty w_0(p(t), R) f^V(R) dR. \qquad (8)$$

According to Eqs. (4), (7), and (8), at $t < \tau_p$, the potential barrier at nonzero excess pressure is determined by the competition between a change in the surface energy $\delta\varepsilon$ of liquid in the pore and the work necessary for emptying the pore with volume V at excess pressure $p(t)$. At $t = \tau_p$, the excess pressure vanishes

and the potential barrier for liquid extrusion is determined by competition between the energy $\delta\varepsilon_1$ of interaction of the liquid and skeleton of the porous medium and the energy $\delta\varepsilon_{int}$ of the effective "multiparticle interaction" of the liquid cluster in the pore and liquid clusters in the neighboring pores. According to Eq. (4), liquid clusters for which the energies of the "multiparticle interaction" with liquid clusters in the neighboring pores are $\delta\varepsilon_{int} > 0$ and $\delta\varepsilon_{int} > |\delta\varepsilon_1|$ form an initial metastable state of the system at $t = \tau_p$ and $p = 0$, which corresponds to the bound states of interacting local configurations of filled pores [62].

3.2. Relaxation and Decay of the Metastable State at $\theta > \theta_c$

Now let us determine the character of relaxation of this state upon pressure release, that is, calculate $\theta(t)$ at $t > \tau_p$ for $p = 0$ and $\theta > \theta_c$. In this case, the system contains a percolation cluster of filled pores through which the liquid can flow out of the porous medium. According to Eq. (5), the effective multiparticle interaction of the liquid cluster and those in neighboring pores is nonzero and is attractive for a fraction of these pores obeying the condition $\delta\varepsilon_{int} > |\delta\varepsilon_1|$. According to Eqs. (2)–(4), the time of liquid extrusion from the pore in a metastable state is

$$\tau = \tau_0 \exp(-\delta\varepsilon(R,\theta,T)/T), \quad \tau_0 \sim 1/R. \quad (9)$$

This time is determined by the degree of filling θ of the porous medium in the metastable state and depends on the pore radius R and temperature T.

Following [62], let us introduce a distribution function $F(t)$ of the times of liquid extrusion from the pores with radius R and volume $V = (4\pi/3)R^3$. This function determines the fraction $d\theta(t)$ of pores from which the liquid was extruded within the time dt: $d\theta(t) = F(t)dt$. For a nonrandom period of extrusion time τ, we have $F^V(t) = \delta(t - \tau)$ where $\delta(t)$ is the Dirac delta function. In a porous medium, pores with various volumes are present with a probability determined by the corresponding distribution function. Then, according to Eq. (9), the barrier $\varepsilon(R, \theta)$, pre-exponential factor $\tau_0(R)$, and extrusion time $\tau(R)$ are random functions. In this case, the distribution function $F^V(t)$ of pore volumes with respect to the times of liquid extrusion can be written as

$$F^V(t) = \int_0^\infty \delta(t - \tau(R))f^V(R)dR, \quad (10)$$

where $\tau(R)$ is given by relation (9) and $f^V(R)$ is the pore volume distribution function normalized to unity. Equations (4), (9), and (10) imply that the liquid is not extruded from all pores within the same time and the number of clusters involved in this relaxation process depends on the time. As will be shown below, this circumstance can lead to the power character of relaxation of the metastable state.

According to Eq. (10), the function $F^V(t)$ determines fraction $\theta(t)$ of the volume of pores from which the liquid was extruded for a time interval t:

$$\int_0^t d\tau F^V(\tau) = \theta(t). \quad (11)$$

With the aim of describing the relaxation of a metastable state formed at $t = \tau_p$, let us count the relaxation time from this moment. Then, if the degree of filling of the medium at the initial time (moment of the metastable state formation) is $\theta(0) = \theta_0$, the volume fraction of pores in which the liquid is retained at time t is determined as

$$\theta(t) = \theta_0 \int_t^\infty dt F^V(t). \quad (12)$$

Calculating integral (12), we find that distribution function $F^V(t)$ has the following form:

$$F^V(t) = f^V(R(t))\frac{dR(t)}{dt}, \quad (13)$$

where $R(t)$ is a solution of the equation

$$\tau(R(t)) = t. \quad (14)$$

In order to solve Eq. (14), note that the metastable state consists of the pores with radii $R < R^*$, where R^* is determined by Eq. (6). In the case of pore volume distribution $f^V(R)$ with the total relative width $\Delta R/\bar{R} < 0.5$, about 90% of the volume belongs to pores with radii $R < \bar{R} + \Delta R$. Therefore, about 10% of the liquid is in pores with radii $R > \bar{R} + \Delta R$. Liquid clusters in the pores with radii $R > R^*$ do not participate in the metastable state, and the liquid from these pores flows out during a hydrodynamic time of about τ_0. For this reason, it will be assume for simplicity that the distribution function of pores with liquid clusters in the metastable state is constant for $0 < R < R^*$ and is zero for $R > R^*$. Then, with allowance for the normalization, the pore volume distribution function $f^V(R)$ in this approximation can be written as follows:

$$\tilde{f}^V(R) = \frac{1}{R^*}\int_0^{R^*} f^V(R)dR \quad \text{for} \quad 0 < R < R^*,$$
$$f^V(R) = 0 \quad \text{for} \quad R > R^*. \quad (15)$$

Analysis shows that the barrier $\varepsilon(R, \theta)$ for pores with radii in this interval is a smooth function of R. Then, in the interval of radii of the pores constituting the metastable state ($0 < R < R^*$), the characteristic extrusion time $\tau(R)$, according to Eqs. (13) and (14), can be expressed as follows:

$$\tau(R) = \tau_0 \left(\frac{\bar{R}}{R}\right) \exp\left(\frac{\delta\varepsilon}{T}\right)$$

$$= \tau_0 \left(\frac{\bar{R}}{R}\right) \exp\left(\frac{\varepsilon_{max}}{T}\right) \exp\left(\frac{\delta\varepsilon - \varepsilon_{max}}{T}\right)$$

$$\approx \tau_0 \exp\left(\frac{\varepsilon_{max}}{T}\right) \exp\left(-\frac{\delta\varepsilon''(R - R_{max})^2}{2T} - \ln\left(\frac{R}{\bar{R}}\right)\right)$$

$$\approx \tau_0 \exp\left(\frac{\varepsilon_{max}}{T}\right) \exp\left(-\ln\left(\frac{R}{\bar{R}}\right)\left(\frac{\delta\varepsilon''(\Delta R)^2}{2T \ln(1 + \Delta R/\bar{R})} + 1\right)\right)$$

$$= \left(\frac{\bar{R}}{R}\right)^{\beta} \tau_0 \exp\left(\frac{\varepsilon_{max}}{T}\right), \qquad (16)$$

$$\beta = 1 + \frac{\delta\varepsilon''(\Delta R)^2}{2T \ln(1 + \Delta R/\bar{R})},$$

$$\delta\varepsilon'' = \left(\frac{d^2\delta\varepsilon(R)}{dR^2}\right)_{R = R_{max}}.$$

Here, $\varepsilon_{max}(\theta)$ is the maximum height of barrier $\varepsilon(R, \theta)$ given by formula (4) and τ_0 is the hydrodynamic time of liquid extrusion from pores of the medium, which is determined by Eqs. (2) and (3). Using Eqs. (4) and (16), exponent β at the ratio $\Delta R/\bar{R}$ can be expressed as

$$\beta = 1 + (2 - \gamma)\frac{\Delta R}{\bar{R}}\frac{\varepsilon_{max}}{T}, \qquad (17)$$

where γ is the exponent in coefficient $\eta(R)$ of the pore connectivity [69].

Using relation (13), pore volume distribution function (15), and Eqs. (12) and (13), the time variation of $\theta(t)$ at $t > \tau_p$ can be described as

$$\theta(t) \sim \theta_p \left(\frac{\tau_{q1}}{t}\right)^{\alpha},$$

$$\alpha = \left\{1 + (2 - \gamma)\frac{\Delta R}{\bar{R}}\frac{\varepsilon_{max}}{T}\right\}^{-1}, \qquad (18)$$

$$\tau_{q1} \sim \tau_0 \exp\left(\frac{\varepsilon_{max}}{T}\right), \quad \theta_p = \frac{\bar{R}}{R^*}\int_0^{R^*} dR f^V(R).$$

It follows from Eqs. (18) that the volume fraction of retained liquid occurring in the metastable state at $t > \tau_p$ decreases according to a power law with exponent α and characteristic time $\tau_{q1} \sim \tau_0 \exp(\varepsilon_{max}/T)$.

Equations (4) and (6) show that the values of $R^*(z, \theta)$ and $\varepsilon_{max}(z, \theta)$ decrease with decreasing degree of filling θ because of reduction in the energy of multiparticle attraction between local configurations [25]. Therefore, as the degree of filling θ decreases according to Eq. (18), the regime of relaxation exhibits a change. The relaxation of the metastable state by power law (18) with an exponent of $\alpha \ll 1$ for $\theta \sim 1$ at low temperatures (for which $\Delta R \varepsilon_{max}/\bar{R}T \gg 1$) changes

(for $\Delta R \varepsilon_{max}/\bar{R}T < 1$) to accelerated relaxation with $\alpha \sim 1$ and characteristic relaxation time

$$\tau_{q1} \sim \tau_0 \exp\left(\frac{\varepsilon_{max}}{T}\right) \sim \tau_0 \exp\left(\frac{\bar{R}}{\Delta R}\right) < 1000\tau_0 \sim 100\,\text{s}.$$

This corresponds to decay of the metastable state. It follows from Eq. (18) that the decay of the metastable state begins at times for which the degree of filling $\theta(t)$ is such that $\Delta R \varepsilon_{max}/\bar{R}T \sim 1$.

Relations (18) also indicate that the power-law dependence of $\theta(t)$ describing the relaxation and decay of the metastable state is related to the total width $(\Delta R/\bar{R})$ of pore size distribution in the medium and to the interaction of local configurations, the maximum energy ε_{max} of which determines both the characteristic relaxation and decay time τ_{q1} and exponent α.

3.3. Discussion of Results

Let us consider the time variation of the volume of liquid retained in the porous medium during the formation, relaxation, and decay of the metastable state. It follows from Eq. (8) that time variation of the volume fraction of retained liquid for $t < \tau_p = 10$ s is determined by Eqs. (2), (4), and (7). Relations (4) and (5) give the potential barrier for liquid extrusion from a pore of radius R in the porous medium filled with the nonwetting liquid at pressure p. Estimations show that, at a temperature below the dispersion transition temperature ($T = 277$ K $< T_d = 284$ K), the maximum barrier for the system under consideration in the absence of excess pressure ($p = 0$) amounts to $\varepsilon_{max} \geqslant 0.8$ eV. At excess pressures $p > 200 \times 10^5$ Pa, the energy barrier for liquid extrusion from pores in the medium with pore volume distribution function $f^V(R)$ (Fig. 7) is $\delta A > 4$ eV. Estimation of the time of liquid extrusion from pores using relations (2) and (4) in this case yields $\tau > 10^{33}$ s. As the excess pressure decreases to $p \sim 100 \times 10^5$ Pa, the barrier δA for liquid clusters in the pores with $R > R_l^*$ becomes negative (Fig. 7), which implies that liquid flows out of these pores for a hydrodynamic time of $\tau \sim 10^{-1}$ s. As the pressure is released, the R^* vale decreases and the number of pores from which the liquid can flow out increases. According to Eqs. (6) and (8), the volume of liquid extruded at zero excess pressure can be expressed as

$$\theta_s = \int_{R^*}^{\infty} f^V(R)dR. \qquad (19)$$

An increase in temperature leads to a decrease in the R^* value. According to Eq. (19), this results in an increasing amount of liquid extruded during the time of excess pressure release ($t = \tau_p$) and, hence, a decreasing amount of liquid retained in the porous medium at this time.
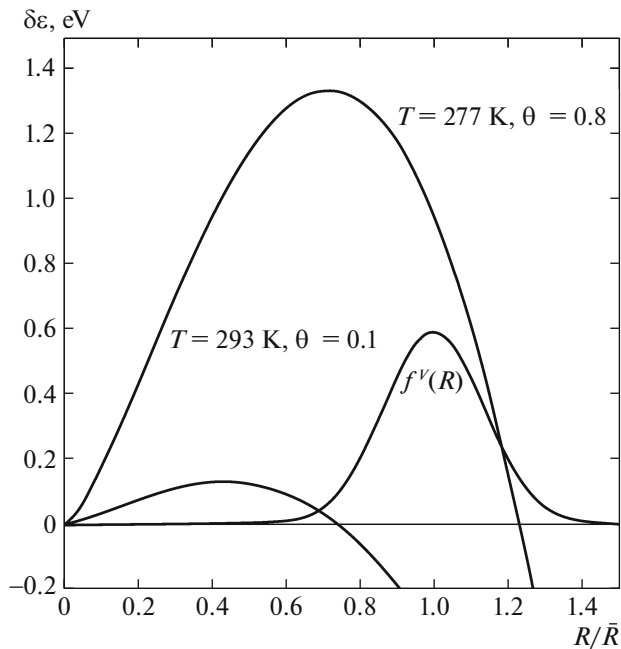
Fig. 8. Potential barrier $\delta\varepsilon$ vs. pore radius R for system studied at time instant $t = \tau_p = 10$ s at temperatures $T = 277$ and 293 K.

Equations (4) and (8) indicate that no extrusion of liquid from a filled porous medium takes place when the excess pressure decreases from about $p = 200 \times 10^5$ Pa to a level of 10^7 Pa, the amount of liquid retained in the medium upon the release of excess pressure can be estimated using relation (19) with R^* determined by formula (6). Estimate made with allowance for the surface tension $\sigma(T)$ [71], $\delta\sigma$, and its temperature dependence (determined as described in [57]) give $1 - \theta_s(T = 277$ K$) \sim 0.15$ and the fraction of the volume of retained liquid $1 - \theta_s(T = 289$ K$) \sim 0.9$. These values are close to the corresponding experimental data on the fraction of retained liquid at $t = 10$ s for the same temperatures ($1 - \theta_s \sim 0.1$ and 0.8, respectively).

It follows from Eqs. (4) and (9) that the character of relaxation of the state formed upon reduction of the excess pressure is determined by the potential barrier $\delta\varepsilon$. Figure 8 shows the plot of $\delta\varepsilon$ versus pore radius R for the system under consideration at the moment of time $t = \tau_p = 10$ s at temperatures $T = 277$ and 293 K, calculated using Eq. (4) with the same parameters $\sigma(T)$, $\delta\sigma$, $\bar{R}$, R_0, z, and φ as those indicated in Fig. 7. As can be seen from Fig. 8, the potential barrier $\delta\varepsilon$ decreases with increasing temperature and decreasing degree of filling. At $T = 293$ K and $\theta_0 = 0.1$ (Fig. 4), the barrier is lower than or comparable with the temperature for all pores. In this case, $\theta < \theta_c$ and only separate clusters of filled pores are formed in the medium, so that there are no pathways of liquid flow out via filled pores. A possible mechanism of liquid extrusion from

the clusters of filled pores is based on evaporation followed by condensation at the boundaries of porous granules and the bulk liquid.

For $T = 277$ K at time instant $t = \tau_p$ corresponding to $\Delta p = 0$, the initial degree of filling is $\theta > \theta_c$ (Fig. 4) and the potential barrier for liquid extrusion is determined by competition between the energy $\delta\varepsilon$ of interaction of the liquid and skeleton of the porous medium and the energy $\delta\varepsilon_{int}$ of the effective multiparticle interaction of a liquid cluster in the pore and liquid clusters in the neighboring pores. For pores with radii $R < R^*$ in a medium at $\theta \sim 0.8$, the energy of the effective multiparticle interaction of a liquid cluster in the pore and liquid clusters in the neighboring pores is $\delta\varepsilon_{int} > 0$. Therefore, it is possible to assume that the interacting local configurations of a pore and its environment are condensed and form a metastable state of the entire system of clusters that decays according to power law (18) with a characteristic time of $\tau_{q1} \sim \tau\exp(\varepsilon_{max}/T)$. For $\tau_0 \sim 0.1$ s and $\varepsilon_{max} \sim 0.5$ eV, this characteristic time at $T = 277$ K is about $\tau_{q1} \sim 10^5$ s. Relation (18) also shows that exponent α for narrow distributions with $\Delta R/\bar{R} = 0.1$ at these parameters is $\alpha \sim 0.1$.

Decay of the metastable state according to Eqs. (18) is accompanied by a decrease in the degree of filling θ, which leads to a decrease in ε_{max} and an increase in α. Accordingly, the decay rate increases in the course of this process. Equations (18) also indicate that this decay begins at a time for which $\Delta R \varepsilon_{max}/\bar{R} T \sim 1$. Estimations for $\Delta R/\bar{R} \sim 0.1$ and $T = 277$ K give the decay onset time exceeding 10^4 s, which agrees with the experimental data (Fig. 4). According to Eqs. (18), the maximum volume fraction θ_p of pore configurations occurring in a metastable state is determined by the integral of the pore volume distribution function

$$\theta_p \sim \int_0^{R^*} dR f^V(R)$$

For a narrow volume distribution of pores with $\Delta R/\bar{R} \sim 0.1$, this fraction amounts to $\theta_p \sim 0.8$.

The relaxation of a metastable state of interacting local configurations of filled pores continues as long as a percolation cluster of filled pores exists in the system. The lifetime of this cluster can be estimated from Eq. (18) by equating the degree of filling to the percolation threshold: $\theta(t) = \theta_c$. Hence it follows that the lifetime of the percolation cluster of filled pores is $t_p \sim \tau_{q1}(\theta_p/\theta_c)^{1/\alpha}$. For $\alpha \sim 0.2$, $\theta_p \sim 0.8$, $\theta_c \sim 0.1$, and allowance for a change in the degree of filling during decay of the metastable state, this time is $t_p \sim 10^6$ s. At a degree of filling below the percolation threshold ($\theta < \theta_c$), only separate clusters consisting of filled pores are formed in the porous medium. A possible mechanism of liquid extrusion from these clusters is based on the
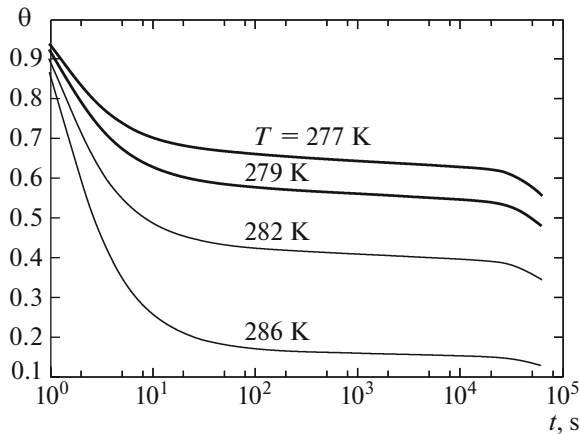
Fig. 9. Qualitative time dependences of volume fraction of retained liquid at $T < T_d = 284$ K and $T = 286$ K, calculated using Eqs. (7), (8), and (18).

evaporation of liquid [58, 59]. Considerations analogous to those used in deriving Eqs. (16) and (18) in this case lead to a logarithmic law of liquid extrusion.

When the excess pressure is reduced from $p > 200 \times 10^5$ Pa to $\sim 10^7$ Pa, liquid clusters in all filled pores of the water–L23 system occur in states with an extrusion barrier $\delta A \sim 4$ eV. The time of liquid extrusion from these states is $t > 10^{33}$ s. Therefore, during pressure release to 10^7 Pa, no extrusion of liquid from the porous medium should take place.

As the excess pressure is further decreased to $p < 10^7$ Pa, pores appear for which the extrusion barrier δA is either negative of comparable with the temperature. From these pores, liquid can flow out within hydrodynamic time τ_0 and, hence, extrusion must be observed during the excess pressure reduction to zero. As the excess pressure approaches zero, the number of such pores increases.

Figure 9 shows the qualitative time dependences of the volume fraction of retained liquid at various temperatures, which were calculated using Eqs. (7), (8), and (18). As can be seen, variation of the excess pressure from 10^7 Pa to zero for 10 s at temperatures $T < T_d = 284$ K leads to a decrease in the degree of filling from $\theta = 1$ to $\theta > \theta_c$, which is accompanied by the decay of weakly bound states and the formation of an initial metastable state of the liquid confined in pores. The relaxation of this metastable state takes place within $t = 100–6000$ s and obeys the power law $\theta(t) \sim t^{-\alpha}$ described by Eq. (18) with an exponent of $\alpha \sim 0.1$. At $t > 10^4$ s, the metastable state exhibits decay (see Fig. 9) and the exponent increases up to $\alpha \sim 0.3$. Figure 9 also shows that the calculated time dependence $\theta(t)$ describes the experimental data qualitatively well (Fig. 3).

A decrease in the excess pressure to zero at temperatures $T > T_d = 284$ K leads to a decrease in the fraction of retained liquid due to the decay of weakly bound states from $\theta = 1$ to degrees of filling below percolation threshold θ_c. The percolation cluster of filled pores disappears and the liquid extrusion mechanism changes to the slower process of evaporation and condensation. Accordingly, the value of exponent α at $T > 284$ K must decrease with increasing temperature. Thus, the increase in α with temperature at $T < T_d = 284$ K (related to the decrease in the potential barrier for liquid extrusion) changes by its decrease with increasing temperature at $T > T_d = 284$ K. This leads to the appearance of a maximum on the temperature dependence of α, in agreement with the experimental data.

The slow relaxation and decay of a metastable state of the nonwetting liquid confined in pores of the medium have been described using the mean-field approximation and are related to the appearance of local configurations of liquid clusters in confinement and their interaction inside an infinite percolation cluster of filled pores. This approach allowed us to qualitatively explain the observed power-law relaxation of $\theta(t)$ and the crossover transition to a power dependence with greater exponent. The passage from temperatures below the dispersion transition temperature ($T < T_d$) to those above the transition temperature ($T > T_d$) leads to a change in the transport conditions. Indeed, at $T < T_d$ and $\theta > \theta_c \sim 0.2$, liquid can flow out from filled pores via the infinite percolation cluster, while the transport at $T > T_d$ proceeds by the evaporation–condensation mechanism. This can be responsible for the change in the relaxation law during the dispersion transition.

Thus, the results of our study of the relaxation of dispersed confined incompressible liquid (water) in a disordered porous medium (hydrophobized silica gel L23) provide a self-consistent statistical pattern of this process, which is based on the notion of local metastable cluster configurations. The system of a disordered porous medium containing clusters of a nonwetting liquid confined in pores has a degenerate ground state characterized by the existence of an infinite fractal percolation cluster of filled pores. This approach makes it possible to describe the intrusion of the liquid and its extrusion during relaxation of the metastable nonergodic state [25, 26]. The established power law of relaxation and dependence of the volume of confined liquid on the degree of filling implies that both the confinement and dispersion transition are related to the interaction of liquid clusters in neighboring pores. Using the proposed mean-field approximation, it is possible to estimate the energy barrier of metastable states of the confined liquid and provide a qualitative description of time variation of the volume of confined liquid.

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