PHYSICAL REVIEW E **93**, 022142 (2016)

Anomalously slow relaxation of interacting liquid nanoclusters confined in a porous medium

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(Received 5 August 2014; revised manuscript received 29 October 2015; published 29 February 2016)

Anomalously slow relaxation of clusters of a liquid confined in a disordered system of pores has been studied for the (water-L23 nanoporous medium) system. The evolution of the system of confined liquid clusters consists of a fast formation stage followed by slow relaxation of the system and its decay. The characteristic time for the formation of the initial state is $\tau_p \sim 10$ s after the reduction of excess pressure after complete filling. Anomalously slow relaxation has been observed for times of 10^1–10^5 s, and decay has been observed at times of $>10^5$ s. The time dependence of the volume fraction θ of pores filled with the confined liquid is described by a power law $\theta \sim t^{-\alpha}$ with the exponent $\alpha < 0.15$. The exponent α and temperature dependence $\alpha(T)$ are qualitatively described theoretically for the case of a slightly polydisperse medium in a mean-field approximation with the inclusion of the interaction of liquid clusters and averaging over various degenerate local configurations of clusters. In this approximation, slow relaxation is represented as a continuous transition through a sequence of metastable states of the system of clusters with a decreasing barrier.

DOI: 10.1103/PhysRevE.93.022142

I. INTRODUCTION

In recent years, to describe the state of relaxation of disordered media such as glasses, colloids, polymers, and other granular media, different phenomenological models have been actively used. Such models include the shear transformation zone (STZ) [1–5], dynamic heterogeneity (DH) [6–8], random first-order transition theory (RFOT), topological bond-oriented local configuration [1,9–14], etc. (see, e.g., [1,6,15–18]). These models involve local structures (configurations), and they are used to describe states and relaxation of glasses, colloids, polymers, and loose media, as well as liquid-glass transitions and the sol-gel process resulting in the appearance of random order. According to [1,19,20], these media are nonergodic and are characterized by an anomalously slow relaxation of local nonequilibrium states, which is phenomenologically described by a stretched exponential relaxation law [1,13,21,22]. Anomalously slow relaxation means that the system cannot necessarily reach an arbitrary point in the phase space during a large observation time smaller than the lifetime of the states [1]. Anomalously slow (power-law) relaxation in phenomenological models of disordered media is attributed to the formation and decay of metastable states.

Disordered porous media constitute a particular case of disordered media. Their structure is studied by gas adsorption-desorption and mercury porometry methods. In this work, it is shown that the properties of disordered porous media can be investigated through the states of a nonwetting liquid confined in the disordered structure of pores after the removal of excess pressure [23–25].

A porous medium immersed in a nonwetting liquid can be filled with this liquid only with an excess pressure above a certain critical value, which can be estimated by the Laplace formula. After the subsequent removal of excess pressure, such a system can be in an unstable state, because surface forces tend to push a nonwetting liquid out. These phenomena are identified in numerous studies of the intrusion-extrusion hysteresis [26–37].

On the other hand, confinement of a fraction of the liquid or the entire liquid volume after the removal of excess pressure is observed for many nonwetting liquids and disordered porous media. The confinement of the liquid was detected when studying intrusion-extrusion for water, aqueous solutions of salts and organic substances, mercury and other metals, Wood's alloy, hydrophobized silica gels KSK-G, PEP 100, PEP 300, Fluka 60, Fluka 100, C8W (Waters), and Vycor and PG porous glasses [26–40]. These media differ in the degree of hydrophobicity, porosity, average pore size (in the range 0.5–20 nm), and average granule size (in the range 10–100 μm), and the width of the pore size distribution. The confinement effect is not related to a phase change. Indeed, according to [41,42], at the radius of pores $\overline{R} > 1$ nm and $T > 273$ K, the properties of the liquid in confinement do not differ from the properties of the bulk liquid. The confined liquid can remain in a porous medium for hours, days, and months. For the (mercury-porous glass) system, the weight of porous glass samples with confined mercury and the results of neutron scattering experiments did not change over several months [41]. For other systems consisting of mercury and Vycor and PG porous glasses and silica gels, the volume of the confined liquid depends on the extrusion time and the size of granules [43].

Investigations indicate that the volume fraction of the confined liquid θ can be from a few percent to 100% [26,27,34,37,38,40,44,45]. In particular, the L23-water system has close to 100% liquid confinement at $T = 279$ K, which is reduced to only 5% for a small temperature change of $\Delta T \approx 10$ K. If the fraction of filled pores is above the percolation threshold θ_c ($\theta_c = 0.15$–0.35, depending on the model of the porous medium [46,47]), the confined liquid can remain in the porous medium for an observation time of 10–10^5 s, although the liquid can be extruded from the sample through filled pores, which form an "infinite" percolation cluster at $\theta > \theta_c$. If θ is below the percolation threshold, $\theta < \theta_c$, only isolated clusters of filled pores are formed in the porous medium. Then, there are no paths for extrusion of liquid from most

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clusters through filled pores to the boundary of the sample. A possible mechanism for extrusion of liquid from clusters is recondensation, i.e., capillary evaporation and subsequent capillary condensation at the (porous medium–surrounding liquid) interface. Capillary condensation and capillary evaporation constitute a mechanism considered as responsible for transport in experiments on adsorption-desorption of gases in porous media [48]. In such experiments, a porous medium is placed in a gas atmosphere and the mass of the adsorbed gas is measured as a function of pressure near saturated vapor pressure. In view of a low density of the gas as compared to the density of the liquid [$\rho_g \sim (10^{-4}\text{–}10^{-3})\rho_l$], under equal conditions otherwise, the flux of the gas is much smaller and the characteristic adsorption-desorption time in such experiments is much larger than the respective values in the case of the transport of liquid through liquid-filled pores forming an "infinite" percolation cluster. The characteristic time in experiments on the adsorption-desorption of gaseous nitrogen at $T = 77$ K is of the order 10^4–10^5 s, whereas for intrusion-extrusion of the nonconfined fraction of the liquid it is ~0.1 s [49].

Thus, it can be expected that there are two different scenarios of relaxation after the filling of the porous medium and the subsequent removal of excess pressure. In the first scenario, most of the liquid is in an unstable state and can be extruded from the porous medium at a characteristic hydrodynamic time of ~0.1 s. The remaining part with the fraction of filled pores below the percolation threshold $\theta < \theta_c$ forms clusters of filled pores surrounded by empty pores. The characteristic time of the extrusion of the liquid from these pore clusters should be determined by the process of capillary evaporation of the liquid from the surface of menisci in filled pores and capillary condensation on the surface of menisci with nearly identical curvature at the interface between the porous medium and the bulk liquid. Consequently, the mass flow in this process is expected to be much smaller and the time is expected to be much larger than for a hydrodynamic flow of liquid through filled pores. In the second scenario, a fraction of the liquid can be in an unstable state and can be extruded in a hydrodynamic time of ~0.1–1 s through filled pores of the "infinite" percolation cluster. In this work, we study the process of extrusion of the confined liquid for the degree of filling θ above the percolation threshold θ_c. Relaxation at $\theta < \theta_c$ can be described within the evaporation-condensation mechanism considered in Ref. [45].

In Refs. [23,25], it was found that the volume of the confined liquid in the systems consisting of water and the L23 or Fluka 100 C18 porous medium depends critically both on the initial degree of filling and the temperature (dispersion transition). These properties cannot be explained through intrusion-extrusion of the liquid from individual pores based on the Laplace relation and a phenomenological contact angle [40,50]. These dependences mean that the behavior of a fraction of the nonwetting liquid can be attributed to the interaction between liquid clusters in neighboring pores [51]. The lattice-gas model was used in Refs. [52,53] to describe the state and relaxation of an ensemble of liquid clusters in pores. Such a model allows the inclusion of interaction between clusters for a random distribution of neighboring pores. Transport in such a model is considered as diffusion transport of a vapor from a filled pore to a neighboring empty pore. This approach describes states and relaxation at the adsorption-desorption of the gas in terms of capillary condensation and capillary evaporation in the porous medium immersed in a gas atmosphere [54]. The slowing down of the process of desorption in the hysteresis region observed in Ref. [55] for the system of cyclohexane in a Vycor porous medium is explained within the lattice-gas model by the slowing down of the diffusion of the vapor as a result of the fragmentation of the condensed liquid. The numerical Monte Carlo study of the lattice-gas model with the Glauber-Kawasaki algorithm under the assumption of diffusion transport of the vapor through neighboring empty pores showed that the volume of the remaining liquid increases with a decrease in the observation time [26].

The confinement of the nonwetting liquid in the disordered structure of pores and the kinetics of the dispersion transition were described in Ref. [56]. Within such an approach, the confinement and (possible) extrusion of the liquid were described for what may be called the ground state of the disordered porous medium-water system, which is characterized by the formation of the "infinite" fractal percolation cluster of filled pores. The observed confinement of the liquid is explained by the transition of a fraction of the liquid to a metastable state at excess pressure and the subsequent removal of excess pressure. The energy barrier of the metastable state is determined as the difference between the surface energy of a liquid cluster in a pore with the frame of the medium, which "extrudes" the nonwetting liquid, and the surface energy liquid cluster in the pore with liquid clusters in neighboring pores (multiparticle interaction).

For the disordered porous medium partially filled with liquid, the arrangement of filled and empty pores is random both on the fractal shell of the percolation cluster of filled pores and inside the percolation cluster. Consequently, the energy barrier of the metastable state forms a random potential profile in the space of the porous medium on the shell and in the volume of the percolation cluster of filled pores. The extrusion of the liquid from pores is the process of overcoming a set of maxima of the potential profile. During the process of extrusion of the liquid, the degree of filling of pores decreases and the percolation cluster "is contracted." This can accelerate the extrusion of the confined liquid because of a decrease in Ref. θ (a decrease in the number of neighboring filled pores) and a decrease in the energy of the "multiparticle interaction."

A description of the relaxation of the metastable state of the confined liquid based on the distribution function of filled pores was proposed in Ref. [56]. This description of relaxation is used in this work for a porous medium with a narrow pore size distribution with relative width $\Delta R/R \ll 1$.

The experiments described below were performed in order to test the mechanism proposed in Ref. [56] for the relaxation of the liquid confined in a porous medium immersed in the same liquid at degrees of filling above the percolation threshold. The problem was formulated as follows. We chose the system of water in the Libersorb 23 (L23) disordered nanoporous medium. After complete filling at excess pressure and subsequent removal of excess pressure in this system, two states of the confined liquid are observed at temperatures above and below a dispersion transition temperature $T_d \approx 284$ K. In one of them, the degree of filling with the confined liquid θ at $T < T_d = 284$ K is higher than the percolation threshold θ_c, and the liquid can be extruded. In the other state, the degree of filling with the confined liquid at $T > T_d = 284$ K is $\theta < \theta_c$, isolated clusters of filled pores are in the metastable state, and the extrusion of liquid is only possible through capillary evaporation-condensation at the boundary of the porous medium.

When measuring the time dependence $\theta(t)$, it was necessary to avoid systematic error during continuous determination of θ over long times up to 10^5 s. We have developed and used a method of step-by-step determination of θ at different times (Sec. II). This method made it possible to reproduce and to control the initial state of the confined liquid at times $t > 10$ s larger than the time of spontaneous, barrierless extrusion of a fraction of the liquid at $\theta > \theta_c$.

We have detected an anomalously slow extrusion with the confined liquid fraction θ both above and below the percolation threshold (Sec. II C). In the observation time of this slow relaxation, the experimental data at $\theta > \theta_c$ are described by an inverse power dependence with exponent $\alpha < 0.1$. The exponent α depends on the temperature, reaching a maximum near the dispersion transition temperature $T_d = 284$ K. This can indicate a change in the transport mechanism.

II. EXPERIMENT

A. Porous medium

The experiments were performed with the Libersorb 23 (L23) nanoporous medium. The L23 nanoporous medium is produced from the commercially available silica gel (KSK-G), where the disordered structure of pores is formed in the sol-gel process. The surface of pores of the KSK-G silica gel was modified by alkylsilanes in the laboratory, which was headed by G. V. Lisichkin (Moscow State University), in order to ensure the hydrophobic properties [50,57]. The characteristics of the samples of the L23 porous medium were obtained from the adsorption of nitrogen at an Autosorb IQ (Quantachrome, USA) analyzer for studying low-temperature sorption and a Micro-Ultrapyc 1200e helium pycnometer. The density of the L23 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 $\phi = 0.52$, the specific surface was $S_p = (199 \pm 7)$ m^2/g, and the mean size of the granules of the L23 powder was $\sim$10 μm. The pore volume distribution function as obtained from the classical Barrett-Joyner-Halenda (BJH) method is shown in Fig. 1. This function provides only a qualitative representation of the pore radius distribution. The mean radius of pores is $\overline{R} = (5.0 \pm 0.2)$ nm, the full width at half-maximum (FWHM) of the distribution near the maximum is $\Delta R = (0.4 \pm 0.1)$ nm, and $\Delta R/\overline{R} \leqslant 0.1$. Tails of the distribution are also observed in the regions of large and small sizes of pores. Consequently, since $\Delta R/\overline{R} \ll 1$, the L23 porous medium can be used to test the relaxation model [56]. In this model, the random potential field of the barrier of local metastable states is attributed to the fractality of the "infinite" percolation cluster of pores filled with the trapped liquid. For this model, a power law of relaxation of such states should be observed [56].

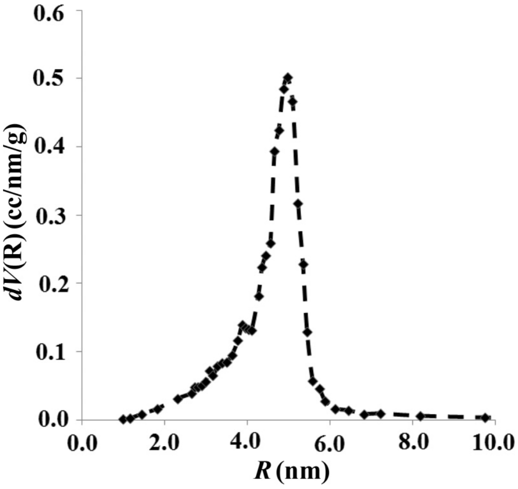

FIG. 1. Pore size distribution function for the Libersorb 23 porous medium according to the BJH method.

B. Measurement procedure

The aim of the performed measurements was to determine the time dependence of the volume fraction of pores θ filled with liquid. Liquid flows from pores rapidly when the imposed pressure is reduced. The extrusion time is less than 1 s [51]. The relaxation of the liquid confined in the porous medium after the initial, rapid, extrusion is studied in this work through the time dependency of θ. The characteristic liquid extrusion time may vary with the mechanism of liquid transport. Transport of liquid may occur as flow through filled pores and through capillary evaporation and subsequent capillary condensation at the interface between the bulk liquid and porous medium immersed in this liquid. The latter mechanism can obviously be efficient in the case of an "infinite" percolation cluster of empty pores, i.e., $\theta < \theta_{c1} = 0.7$–$0.85$ after the initial, rapid extrusion. Therefore, the developed method should ensure the measurement of the volume at the extrusion and evaporation of the confined liquid captured in porous medium after the intrusion-extrusion process. In experiments, it was also necessary to determine the initial state of the confined liquid, the time and conditions of the beginning of relaxation of the state and of the extrusion of the confined liquid from the porous medium, and the possible effect of the prehistory (the formation of the initial state). A particular goal is to experimentally confirm that the properties of the medium remain unchanged under repeated measurements. The determination of the time scales of extrusion and evaporation makes it possible to determine the time interval in which, according to the model [56], the slow extrusion of the liquid (power-law relaxation) should occur.

The method used to measure the volume of the (nonwetting liquid-porous medium) system was similar to mercury [48] or water [50] porometry. A dried and degassed sample of the L23 porous medium with mass up to 6 g held 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 distilled water. A rod 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 chamber was aged at a given temperature for no less than 1 h. The temperature was maintained with an accuracy of ±0.2 K. The chamber was mounted on the bench described in Ref. [27] to allow a given force to be applied to the rod, with measurement of the force and displacement of the rod. All pores were filled because of an increased pressure as the rod was displaced into the chamber. The impermeability of the chamber filled with water and porous sample was ensured by seals. The force (F) acting on the rod was measured by a strain gauge dynamometer CWH-T2 (Dacell, South Korea), and the displacements (l) of the rod were measured by a potentiometric displacement sensor model 8719 (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 $V = lS_r$. Data were recorded from gauges with a frequency of 1 kHz.

The increased pressure resulted in elastic strains of the chamber, liquid, and porous medium. Filling of pores of the L23 porous medium with water was observed only at pressure $>120 \times 10^5$ Pa. This made it possible to determine the effective compressibility of the chamber, as well as the compressibilities of water and the porous medium in additional experiments at pressure $<120 \times 10^5$ Pa; the corresponding data were taken into account when determining the volume of filled pores at a given pressure.

Initially, the porous medium was dried and degassed. We used a step-by-step method to determine the time (t) dependence of the degree of filling (θ) of pores with the confined liquid. The degree θ was determined after the observation time (t_i). Then, the (porous medium–liquid) system was returned to the initial state, and $\theta(t_j)$ was determined at different times t_j, both larger and smaller than t_i. The dependence $\theta(t)$ was obtained by multiple repetition of such a procedure with various t_i values. Each step of the procedure consisted of two successive intrusion-extrusion cycles performed after time t_i. The pressure variations that result from changes in the volume of the L23-water system at $T = 286$ K for two successive cycles at the first step of the measurement are shown in Fig. 2. Changes in the volume of the system because of the compressibility of the liquid, the frame of the porous medium, and the chamber have been subtracted. Dependence **I** corresponds to a decrease in the volume of the empty porous medium at an increase in the pressure in the first cycle. Dependence **I′** corresponds to an increase in the volume at a decrease in the pressure. Three sections can be identified in the dependence $V(p)$. Section **0-1** corresponds to the compression of the empty porous sample, and the slope of this linear section is determined by the compressibility of the empty porous medium. Filling of pores was observed neither in the initial state at atmospheric pressure, $p = (1.00 \pm 0.05) \times 10^5$ Pa, when empty pores can contain saturated water vapor, nor at high pressures up to 120×10^5 Pa at point **1** in section **0-1** when the observation time is smaller than 15 h. Section **1-2** of dependence **I** corresponds to filling of available pores of the empty porous medium. At pressure $P = 450 \times 10^5$ Pa, ≈99.8% of pores are filled. The volume of all filled pores of the sample is equal to the difference $|V_2 - V_1|$. When the pressure decreases below point **3** in dependence **I′**, V decreases, corresponding to the extrusion of the liquid from pores, which is described by dependence **I′**. The main decrease in the quantity V is observed at low pressures comparable with the error of the measurement of the pressure, and the volume of the confined liquid can be determined from the intersection of the dependence $V(p)$ with the y axis only with the accuracy $\delta V/V \sim 1$. For this reason, in the experiments, we determined the volume of pores in two successive intrusion-extrusion cycles.

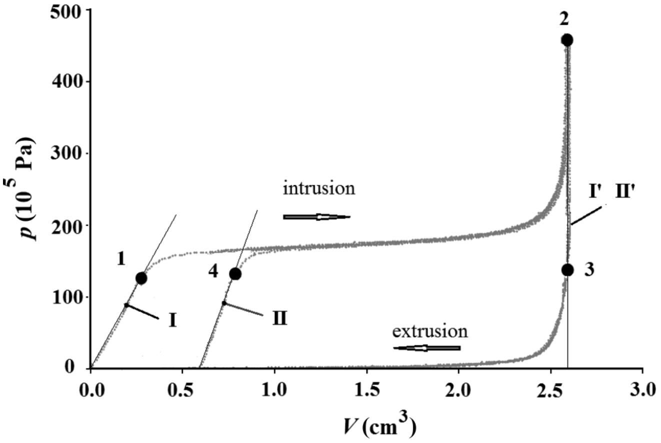

FIG. 2. Pressure as a function of volume change for the L23-water system at $T = 286$ K for two successive cycles. An explanation is given in the main text.

Before repeated filling in the second cycle, some pores contain the confined liquid and, when the pressure in the second cycle increases above point **4** in dependence **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 filled pores after the first cycle, $V_t = (|V_2 - V_1| - |V_2 - V_4|)$. Correspondingly, $\theta = V_t/|V_2 - V_1|$. The relative compressibilities in the sections of filling of the empty porous medium and the partially filled porous medium are almost the same, $(7.5 \pm 0.9) \times 10^{-9}$ Pa^{-1}, within the error of measurements. After the complete filling, the system "forgets" the prehistory of the formation of the preceding initial state and its relaxation, and the initial state of the confined liquid is formed again after the extrusion of a fraction of the liquid (dependence **II′**). Thus, the volume of all empty pores can be determined during the subsequent filling. The volume of pores that remain empty after the extrusion of the liquid in the time interval from the beginning of extrusion in the first cycle (point **3**) to the time of the beginning of filling at the repeated increase in the pressure (point **4**) is determined at repeated filling.

Consequently, V in such a method is determined for the time t passing from the beginning of the extrusion of the liquid in the first cycle when the pressure decreases below point **3**. The time t includes the time t_1 for reaching "zero" excess pressure [i.e., $p = p_{\text{atm}} = (1.00 \pm 0.05) \times 10^5$ Pa] and the time t_i to the beginning of the repeated filling at point **4** in the second cycle. According to [56], spontaneous barrierless extrusion of the unconfined liquid from some pores, as well as extrusion from pores in which the liquid is in a loosely bound state with a low barrier comparable to the temperature, can occur during the time t_1. The height of this barrier can be estimated assuming that $t \sim \tau_0 \exp(E/T)$. At $t_1 \sim 10$ s and $\tau_0 \sim 0.1$ s, $E/T \leqslant 5$. As follows from the estimate given below (see Sec. III C), the volume fraction of pores with the liquid in loosely bound states is several percent. Since the pressure decreasing time $t_1 = 10$ s is much larger than the time of hydrodynamic extrusion of a fraction of the liquid at $\theta > \theta_c$, the decrease in the volume follows the decrease in the pressure. Thus, the initial state of the system is formed in the time fixed in all measurements as $t_1 = 10$ s, and the relaxation of the metastable state of the confined liquid begins after the time t_1. The volume of the confined liquid in the metastable state V_t in the experiments is obtained after the observation time of relaxation (extrusion of the liquid) $t = t_i$. This volume includes the volume V of the liquid remaining after the extrusion in the time interval $t = t_i$, and it does not include the volume of the liquid in these loosely bound states.

To test the reproducibility of the initial state, we performed additional experiments, with multiple measurements of θ at the chosen time $t = t_1 + t_i = 1$ min. It was found that the spread of the measured θ values at $t = 1$ min is smaller than the error of the measurements. Other additional experiments indicated that $\theta(t_i)$ values and the θ value at different time t_j are independent of the sequence of these measurements. Multiple intrusion-extrusion-confinement experiments with the nonwetting liquid at temperatures $T = 277$–293 K including the subsequent removal of the confined water from the L23 porous medium by evacuation drying at $T = 343$ K performed before and after the measurements of $\theta(t)$ confirm that the properties of the porous medium did not change. The specific volume of pores, the pressure at point **1** in Fig. 2, and the pressure at point **3** remained unchanged within the error of measurements after more than 100 identical cycles. This confirms the stability of the hydrophobizing layer on the surface of the L23 porous medium.

C. Experimental results

The dependences $\theta(t)$ for seven temperatures from 277 to 293 K are shown as a log-normal plot in Fig. 3. These experimental values of θ were obtained by the step-by-step method in two intrusion-extrusion cycles with variation in observation time t from 10 to 10^5 s at each step. Points in Fig. 3 represent the results from at least three measurements of θ at each value of time t. The spread of θ values does not exceed the error of the measurement. This confirms the reproducibility of the initial state of the (liquid-disordered porous medium) system at "losing memory" of the preceding states after complete filling in the first and second cycles. The coincidence of θ values can be attributed to the fact that, after complete filling and subsequent removal of excess pressure, the system was in one of the numerous degenerate states with the formation of the "infinite" percolation cluster of filled pores at $\theta > \theta_c$ or empty pores at $\theta < \theta_{c1}$. The degree of filling is the same for all these states.

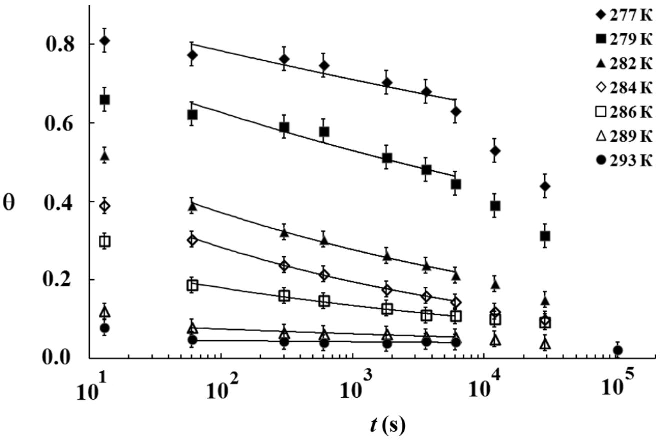

FIG. 3. Dependences $\theta(t)$ at seven temperatures from 277 to 293 K in the time interval from 10 to 10^5 s. Experimental points in comparison with the power-law approximations $\theta \sim t^{-\alpha}$ shown by solid lines in the time interval from 60 to 6×10^3 s.

The (water-L23 porous medium) system undergoes a dispersion transition. With an increase in temperature, the transition from an almost total nonextrusion of the liquid at $T = 277$ K to an almost total extrusion at $T = 293$ K occurs in a narrow temperature range ($\Delta T \approx 10$ K) near a critical temperature.

At temperatures $T = 277$ and 279 K and time of relaxation from 13 to 3×10^4 s, the degree of filling decreases from 0.82 to 0.45 and from 0.65 to 0.35, respectively (see Fig. 3). In this case, $\theta > \theta_c$, where $\theta_c = 0.15$–0.3 is the percolation threshold, and time relaxation occurs in an "infinite" percolation cluster of filled pores. Consequently, the liquid can leave the porous medium via the mechanism of extrusion through filled pores.

At temperatures $T = 289$ and 293 K in the time interval from 13 to 3×10^4 s and from 13 to 10^5 s, respectively, the degree of filling θ of pores with the liquid varies from 0.16 to 0.04 and from 0.08 to 0.02, respectively. At such degrees of filling below the percolation threshold θ_c, the confined liquid is located in pores that form clusters surrounded by empty pores. Therefore, the volume of the confined liquid can decrease via capillary evaporation from the surface of the liquid in clusters of filled pores, diffusion of vapor in the residual gas in the infinite percolation cluster of empty pores, and capillary condensation at the interface between the bulk liquid and granules of the porous medium. Fluxes in such a transport mechanism are small compared to the hydrodynamic flow of the liquid because the density of vapor is much lower (by a factor of 10^3–10^4).

A transition from the "infinite" cluster of filled pores when $\theta > \theta_c$ to individual clusters of filled pores when $\theta < \theta_c$ is consistent with the behavior $\theta(t)$ at temperatures 282, 284, and 286 K. Both the hydrodynamic transport mechanism and the evaporation-condensation transport mechanism are probably of importance under these conditions.

As is seen in Fig. 3, a power-law approximation $\theta \sim t^{-\alpha}$ fits the experimental data only in the range of 60 to 6×10^3 s, probably due to the existence of either an "infinite" cluster of filled pores (temperatures 277–286 K) or an "infinite" cluster of empty pores (temperatures 289 and 293 K) in a given time interval. The spontaneous outflow of liquid through the system of filled pores continues at times up to 60 s, and either the changed transport mechanism or both transport mechanisms are probably active after 6×10^3 s. The experimental data can be described within the error of the measurements by a power law $\theta \sim t^{-\alpha}$ with the exponent α depending on the temperature only in the time interval from 60 to 6×10^3 s.

TABLE I. Values of α.

T (K)	α	$\Delta\alpha$
277	5.20×10^{-2}	6.36×10^{-3}
279	6.70×10^{-2}	6.72×10^{-3}
282	1.13×10^{-1}	4.28×10^{-3}
284	1.61×10^{-1}	2.43×10^{-4}
286	1.53×10^{-1}	2.88×10^{-3}
289	8.42×10^{-2}	5.20×10^{-3}
293	4.00×10^{-2}	3.16×10^{-2}

The temperature dependence of the exponent is shown in Table I. The error $\Delta\alpha$ in the α values corresponds to the confidence parameter R^2 as $\Delta\alpha = \alpha(T)[1 - R^2(T)]$ for the power-law approximation $\theta \sim t^{-\alpha}$.

The large error $\Delta\alpha = 3.16 \times 10^{-2}$ for $T = 293$ K can be due to a change in the relaxation mechanism. Relaxation at $\theta < \theta_c$ occurs via the vapor transport mechanism [36]. In this case, since the hydrodynamic flow time in a channel is independent of the radius of the channel for a Knudsen gas, the relaxation should follow a logarithm rather than a power law because the Knudsen number in the experiments at $p = 10^5$ Pa, $\overline{R} = 4$ nm, and $T \approx 300$ K is Kn >10.

The experiments provide the following conclusions. When the excess pressure was varied from 450×10^5 to $\sim 120 \times 10^5$ Pa, the extrusion of the liquid from the filled porous medium was not observed in the time interval $t = 5$ s for the entire temperature range under study. Extrusion begins at the excess pressure $p < 120 \times 10^5$ Pa. The extrusion of the confined liquid occurs differently at temperatures above and below the dispersion transition temperature $T = T_d \approx 284$ K. At temperatures $T > 289$ K, the degree of filling changes to values below the percolation threshold θ_c in the time $\tau_p = 10$ s after reduction of the pressure from 120×10^5 Pa to zero. In this case, in the time interval from 10 to 10^6 s, the degree of filling θ of pores with the liquid varies from 0.08 to 0.02 according to the power law $\theta \sim t^{-\alpha}$ with the exponent $\alpha \leqslant 0.05$.

At $T < T_d$, partial extrusion of ~20% of the liquid is observed at time $\tau_p = 10$ s after reduction of the pressure from 120×10^5 Pa to zero. The degree of filling for the confined liquid θ is larger than the percolation threshold θ, and fast (at time $\sim\tau_0 \sim 0.1$ s [49]) hydrodynamic extrusion of the liquid through the percolation cluster of filled pores is possible. However, this process does not occur, and the degree of filling at a time from 10 to 6×10^3 s decreases from 0.8 to 0.6 according to the power law $\theta \sim t^{-\alpha}$ with the exponent $\alpha \leqslant 0.2$.

III. STAGES OF RELAXATION

It was argued above that two different relaxation scenarios are possible after the filling of the porous medium and the subsequent removal of excess pressure. At temperatures $T < T_d$, a fraction of the liquid after the removal of excess pressure can be in an unstable state, and it flows out in about $t = 10$ s through filled pores of an "infinite" percolation cluster. Partial extrusion up to 60% of the liquid occurs during this time interval. According to [56], the remaining larger (~80%) part of the liquid in observation times from 20 to 6×10^3 s is in a metastable state and only slowly flows out. At temperature $T = 277$ K, the degree of filling decreases from 0.8 to 0.6 according to a power law $\theta \sim t^{-\alpha}$ with the exponent $\alpha \leqslant 0.2$.

At temperatures $T > 284$ K, most of the liquid, ⩾80%, is in an unstable state and flows from the porous medium in a characteristic time of the removal of excess pressure $t \sim 10$ s. The remaining liquid with the fraction of filled pores below the percolation threshold $\theta < \theta_c$ at times $t \gg 10$ s slowly relaxes according to a power law $\theta \sim t^{-\alpha}$ with a small exponent value $\alpha \leqslant 0.05$.

Thus, it is necessary to describe the process of extrusion of the confined liquid for $t < 10$ s in two different cases: (i) the decay of unstable states of filled pores occurs to θ below the percolation threshold θ, and isolated clusters of liquid-filled pores can be formed; and (ii) the decay of unstable states ends in time $t \sim 10$ s with θ above the percolation threshold θ and results in the formation of a metastable state.

A. Kinetics of the formation of the metastable state

We consider the dynamics of the extrusion of the nonwetting liquid from the nanoporous medium. The porous medium is initially completely filled at excess pressure $p_0 = 450 \times 10^5$ Pa. With a decrease in the pressure to the critical value $p_c \sim 120 \times 10^5$ Pa, the process of extrusion of the liquid from the porous medium begins. The aim is to calculate the time dependence of the volume fraction of the liquid remaining in the porous medium $\theta(t)$ with the reduction of excess pressure $p(t)$ to zero during the pressure reduction time τ_p.

We assume that the disordered nanoporous medium contains pores with different sizes and the porous medium is much larger than the maximum pore, and an infinite percolation cluster of pores is formed. The extrusion of the liquid from the nanoporous medium can occur through two different mechanisms. If θ is above the percolation threshold θ for filled pores, these pores form a connected system of filled pores through which the liquid can be extruded with the characteristic hydrodynamic time $\tau_0 \sim 0.1$ s [49]. If the degree of filling with the confined liquid is $\theta < \theta_c$, connected paths for the extrusion of the liquid are absent and the extrusion of the liquid is possible through capillary evaporation-condensation at the boundary of the porous medium.

The characteristic pressure reduction time in the performed experiments was $\tau_p = 10$ s; consequently, $\tau_p \gg \tau_0$. The process of extrusion of the liquid at pressure variation times $\tau_p \gg \tau_0$ can be considered as a process occurring in a quasistationary medium with excess pressure $p(t)$ decreasing slowly.

According to [25,56], the time of extrusion of the liquid from the pore is given by the expression

$$\tau = \tau_0 \exp(\delta A / T). \tag{1}$$

Here, τ_0 is the hydrodynamic time of extrusion determined by the dynamics of extrusion of the liquid from the porous medium. This time can be estimated as follows. If the liquid is extruded from the pore with radius R through a channel of filled pores with the same radius, $\tau_0 = \frac{4\pi R^3}{3Q(R)}$ [56]. In the case of the flow of liquid through the channel of radius R, $Q(R) \sim R^4$ [58] and $\tau_0 \sim 1/R$.

The expression for δA in the case of a spherical pore with radius R can be represented in the form [56]

$$\begin{aligned} \delta A(R,\theta) &= pV + \delta\epsilon, \\ \delta\epsilon &= \delta\epsilon_1(R) + \delta\epsilon_{\text{int}}(R,\theta), \\ \delta\epsilon_1(R) &= -\delta\sigma[1-\eta(R)]S, \\ \eta(R) &= \frac{\langle S_m(R)\rangle}{S}, \\ \delta\epsilon_{\text{int}}(R,\theta) &= \sigma W(z,\theta)\eta(R). \end{aligned} \tag{2}$$

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

According to Eq. (1), δA serves as the potential barrier for the extrusion of the liquid from the pore. If $\delta A < 0$, the characteristic extrusion time τ is determined by the hydrodynamic time τ_0 for the motion of liquid in the porous medium. If $\delta A > 0$, the characteristic liquid extrusion time is determined by the extrusion potential barrier δA. The characteristic liquid extrusion time in this case can be much larger than the hydrodynamic time $\tau \gg \tau_0$ when the barrier is $\delta A > T$. The barrier δA includes the work (pV) done by the system during an increase in its volume by the volume V of the pore at a pressure p and a change in the surface energy $\delta\epsilon$ of the liquid in the pore at the extrusion of the liquid. This change in energy $\delta\epsilon$ should include, first, a change in energy $\delta\epsilon_1$ at the extrusion of the liquid from the pore associated with the interaction of the liquid with the frame of the porous medium, and second, a change in the energy of the environment of the pore $\delta\epsilon_{\text{int}}$ from which the liquid flows. This is because the extrusion of the liquid from the filled pore results in the formation of menisci in throats connecting this pore to neighboring liquid-filled pores and in the disappearance of menisci in throats connecting this pore to empty pores. As a result, the energy of the liquid in neighboring pores changes. This change in energy depends on the numbers of filled and empty pores in the environment of the pore from which the liquid flows (local configuration), and, therefore, on the degree of filling of the porous medium θ. This can be treated as a "multiparticle interaction" of the liquid in the pore with its environment, which depends on the degree of filling θ.

The function $\eta(R)$ defined as the ratio of the mean area of menisci to the area of the surface of the pore was calculated in Ref. [59], $\eta \sim q(R_0/R)^{-\gamma}$, $\gamma \approx 0.3$, $q \approx 1.0$ [56]. The function $W(z,\theta)$ is defined as the average difference between the number of menisci after and before the depletion of the pore [24], where z is the average number of nearest neighbors.

According to Eq. (2), the energy of the "multiparticle interaction" of the liquid cluster with clusters in neighboring connected pores, together with the surface energy of liquid clusters with the frame of the medium and the work pV, forms the local random profile of a potential barrier for the extrusion of the liquid from the pore in this disordered medium. In view of the dependence of the number of filled (empty) pores on the degree of filling, this barrier can be negative for some pores and the liquid rapidly flows from them [24,56]. The barrier is positive for the other pores and metastable states appear. It follows from Eq. (2) that the energy of the "multiparticle interaction" is positive, $\delta\epsilon_{\text{int}} > 0$, at $\theta_0 \leqslant \theta \leqslant 1$, and it is negative, $\delta\epsilon_{\text{int}} < 0$, at degrees of filling of the porous medium below a certain value $\theta_c < \theta < \theta_0$ [24,56]. According to estimates [23,24], $\theta_0 \approx 0.3$ for a porous medium with a narrow pore size distribution with relative width $\Delta R/\overline{R} \ll 1$.

It follows from Eq. (2) that the potential barrier δA is determined by the pressure p and by the surface energy $\delta\epsilon$ of the liquid in the pore, and it depends on the radius of the pore R. According to Eq. (2), the quantity pV is always positive, whereas the surface energy $\delta\epsilon$ has a maximum $\epsilon_{\max}$ for $R = R_{\max}(z,\theta)$ and can change sign at radii $R^*(z,\theta)$ for which $\delta\epsilon_{\text{int}}(R,\theta) = |\delta\epsilon_1|$. It follows from this condition that

$$R^*(z,\theta) = q^{\frac{1}{\gamma}} R_0 \left(1 + \frac{\sigma}{\delta\sigma} W(z,\theta)\right)^{\frac{1}{\gamma}}, \tag{3}$$

where $R_0 \approx \overline{R}/\overline{z}$ is the minimum size of pores in the pore volume distribution $f^V(R)$. According to Eqs. (2) and (3), the surface energy for $R < R^*(z,\theta)$ is positive, $\delta\epsilon > 0$. In this case, the potential barrier δA is positive at any pressure p. Consequently, the extrusion time from such a state given by Eq. (1) is exponentially large, $\tau = \tau_0 \exp(\delta A/T) \gg \tau_0$, compared to the hydrodynamic time $\tau_0 \sim 0.1$ s.

The surface energy $\delta\epsilon$ for $R > R^*(z,\theta)$ is negative, $\delta\epsilon < 0$. It follows from Eq. (3) that the barrier δA in this case critically depends on the pressure p. The barrier δA is positive, $\delta A > 0$, at pressures $p > p_c = \frac{\delta\epsilon}{V}$, and it is negative, $\delta A < 0$, at $p < p_c = \frac{\delta\epsilon}{V}$. The critical pressure depends on the radius of the pore $p_c(R)$. For this reason, at excess pressure p, the barrier for some pores is negative and, according to Eq. (1), the liquid can flow from these pores in the hydrodynamic time $\tau_0 \sim 0.1$ s. The barrier for the other pores is positive, $\delta A > 0$. According to Eq. (1), the extrusion time from such pores can be exponentially large, $\tau = \tau_0 \exp(\delta A/T) \gg \tau_0$.

It follows from Eq. (3) that the quantities $R^*(z,\theta)$ and $\epsilon_{\max}(z,\theta)$ depend on the temperature through the temperature dependence of the surface tension coefficients $\sigma(T)$ and $\delta\sigma(T)$. The analysis shows that the quantities $R^*(z,\theta)$ and $\epsilon_{\max}(z,\theta)$ increase with decreasing temperature and with an increase in the degree of filling θ [24]. Correspondingly, the potential barrier δA also depends on the temperature, increasing with decreasing temperature and with an increase in the degree of filling θ.

The potential barrier δA can be calculated with use of the results [60] for the surface tension coefficient $\sigma(T)$ and its temperature dependence. The surface tension coefficient of water at $T = 293$ K is 75 mJ/m^2 [60]. The quantity $\delta\sigma$ and its temperature dependence for the system under study were determined from the temperature dependence of the extrusion pressure by the method described in Ref. [51]. The $\delta\sigma$ value at $T = 293$ K is 22 mJ/m^2. The quantity $R_0 \sim \frac{\overline{R}}{\overline{z}}$ was estimated within the model of randomly distributed spheres [24,59]. At the porosity $\phi \sim 0.5$ and $\overline{R} \sim 5$ nm, $R_0 \sim 1$ nm.

The energy barrier for extrusion from pores with the distribution function $f^V(R)$ at pressures $p > 200 \times 10^5$ Pa is $\delta A \sim 4$ eV. The reduction of the pressure to $p \sim 100 \times 10^5$ Pa is accompanied by a change in the potential barrier. The potential barrier for extrusion from pores with radius $R > R^*$ disappears, $\delta A(R > R^*) \leqslant 0$.

The dependence of the volume fraction of the liquid remaining in the porous medium at times $t < \tau_p = 10$ s can be calculated taking into account that extrusion at times $\tau_p \gg \tau_0$ can be considered as a quasistatic process at an excess external pressure $p(t)$ decreasing slowly to zero. In this case, following [49], the probability of finding a pore in the filled state at the pressure can be determined as

$$w_0(p(t),R) = \left[1 + \exp\left(\frac{-\delta A(p(t),R)}{T}\right)\right]^{-1}. \quad (4)$$

Then the time dependence of the volume fraction of the liquid remaining in the porous medium upon reduction of the pressure at times $t < \tau_p = 10$ s can be represented in the form

$$\theta(t) = \int_0^\infty w_0(p(t),R) f^V(R) dR, \quad (5)$$

where $f^V(R)$ is the pore volume distribution function.

According to Eq. (5), the time dependence of the volume fraction of the remaining liquid at times $t < \tau_p = 10$ s is determined by Eqs. (4) and (5). The potential barrier at nonzero excess pressure $p(t) \neq 0$ is determined by the competition between a change in the surface energy $\delta\epsilon$ of the liquid in the pore and the work necessary for the depletion of the pore. At $t = \tau_p = 10$ s, excess pressure $p(t)$ vanishes and the potential barrier for the extrusion of the liquid is determined by the competition between the energy of the interaction of the liquid with the frame of the porous medium $\delta\epsilon_1$ and the energy of the effective "multiparticle interaction" of the liquid cluster in the pore with liquid clusters in neighboring pores $\delta\epsilon_{\text{int}}$. According to Eq. (2), liquid clusters for which the energy of the effective "multiparticle interaction" with liquid clusters in neighboring pores is positive, $\delta\epsilon_{\text{int}} > 0$, and $\delta\epsilon_{\text{int}} > |\delta\epsilon_1|$ form the metastable state of the system corresponding to the bound states of interacting local configurations of filled pores [56].

B. Kinetics of the relaxation and decay of the metastable state at $\theta > \theta_c$

We now determine the character of relaxation of this state $\theta(t)$ at times $t > \tau_p$ in the absence of excess pressure $p = 0$ and $\theta(t) > \theta_c$. In this case, the system includes a percolation cluster of filled pores through which the liquid flows from the porous medium. According to Eq. (3), the effective "multiparticle interaction" of the liquid cluster with neighboring clusters in pores is nonzero and is attractive at $\theta > \theta_0 \sim 0.2$. This interaction ensures the existence of the metastable state of some pores satisfying the condition $\delta\epsilon_{\text{int}} > |\delta\epsilon_1|$. It follows from Eqs. (1) and (3) that the time of extrusion of the system is

$$\tau = \tau_0 \exp[-\delta\epsilon(R,\theta,T)/T], \ \tau_0 \sim 1/R. \quad (6)$$

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

Following [56], we introduce the distribution function $F(t)$ in the time of extrusion from a pore with radius R and, correspondingly, volume $V = \frac{4}{3}\pi R^3$. This function determines the volume fraction of pores $d\theta(t)$ from which the liquid flows in time $dt \approx d\theta(t) = F(t)dt$.

The relaxation function $F^V(t)$ of this state $\theta(t)$ is normalized to unity, $\int_0^\infty F^V(\tau)d\tau = 1$, and the integral

$$\int_0^t F^V(\tau)d\tau = \theta(t) \quad (7)$$

determines the volume fraction of pores $\theta(t)$ from which the liquid flows in the time interval from zero to t. Since we describe the relaxation of the metastable state formed at the time $t = \tau_p$, we measure the relaxation time from this time. Then, if the medium at the initial time (time of the formation of the metastable state) is filled to the degree of filling $\theta(0) = \theta$, the volume fraction of pores $\theta(t)$ from which the liquid did not flow to the time t is determined by the expression

$$\theta(t) = \theta \int_t^\infty F^V(t)dt. \quad (8)$$

Following [56], we find that the distribution function $F^V(t)$ has the form

$$F^V(t) = f^V[R(t)]\frac{dR(t)}{dt}. \quad (9)$$

Here, $R(t)$ is the solution of the equation

$$\tau[R(t)] = t. \quad (10)$$

Integral (8) of the distribution function given by Eq. (9) determines the time dependence of the volume fraction of liquid in the porous medium in the metastable state.

Following [61,62] and using Eqs. (9) and (10), we obtain $\theta(t)$ for the times $t > \tau_p$ in the form

$$\theta(t) \sim \theta\left(\frac{\tau_q}{t}\right)^\alpha, \quad \alpha = \frac{1}{1 + (2-\gamma)\frac{\Delta R}{\overline{R}}\frac{\epsilon_{\max}}{T}},$$
$$\tau_q \sim \tau_0 \exp\left(\frac{\epsilon_{\max}}{T}\right), \quad \theta_p = \frac{\overline{R}}{R^*}\int_0^{R^*} f^V(R)dR. \quad (11)$$

Here, $\epsilon_{\max}$ is the maximum height of the barrier $\epsilon(R,\theta)$ in Eq. (4), and τ_0 is the hydrodynamic time of extrusion of the liquid from pores of the porous medium [56].

It follows from Eq. (11) that the volume fraction of the remaining liquid in the metastable state at times $t > \tau_p$ decreases according to a power law with the exponent α and characteristic time $\tau_q \sim \tau_0 \exp(\frac{\epsilon_{\max}}{T})$. According to Eqs. (2) and (3), the quantities $R^*(z,\theta)$ and $\epsilon_{\max}(z,\theta)$ decrease with a decrease in θ because of the reduction of the energy of the "multiparticle attraction" between local configurations [24]. For this reason, it follows from Eq. (11) that the regime of relaxation changes with a decrease in the degree of filling $\theta(t)$ due to reduction of $\epsilon_{\max}$. The relaxation of the metastable state according to Eq. (11) with the exponent $\alpha \ll 1$ for degrees of filling $\theta \sim 1$ at low temperatures and $\frac{\Delta R}{\overline{R}}\frac{\epsilon_{\max}}{T} \gg 1$ is replaced at $\frac{\Delta R}{\overline{R}}\frac{\epsilon_{\max}}{T} < 1$ by fast relaxation with the exponent $\alpha \sim 1$ and characteristic relaxation time $\tau_q \sim \tau_0 \exp(\frac{\epsilon_{\max}}{T}) \sim \tau_0 \exp(\frac{\overline{R}}{\Delta R}) < 1000\tau_0 \sim 100$ s. This corresponds to the decay of the formed metastable state. According to Eq. (11), the decay of the metastable state begins at times for which the degree of filling $\theta(t)$ is such that $\frac{\Delta R}{\overline{R}}\frac{\epsilon_{\max}}{T} \sim 1$.

Expression (11) indicates that the power-law dependence $\theta(t)$ for the relaxation and decay of the metastable state is due to the polydisperse distribution $(\Delta R/\overline{R})$ of the porous medium and to the interaction between local configurations.

C. Discussion of the results

We now discuss the time dependences the volume of the liquid remaining in the porous medium at three stages of the formation, relaxation, and decay of the metastable state. It follows from Eq. (5) that the time dependence of the volume fraction of the remaining liquid at times $t < \tau_p = 10$ s is determined by Eqs. (1), (2), and (4).

Estimates show that the maximum value $\epsilon_{\max}$ for the system under study at temperatures below the transition dispersion temperature $T_d = 284$ K is $\epsilon_{\max} \geqslant 0.8$ eV. At excess pressures $p > 200 \times 10^5$ Pa, the energy barrier for extrusion from pores with the pore distribution $f^V(R)$ is $\delta A \sim 4$ eV. In this case, the time of extrusion of the liquid from pores is estimated by Eqs. (2) and (4) as $\tau > 10^{33}$ s. When excess pressure is reduced to $p \sim 100 \times 10^5$ Pa, the barrier δA becomes negative for liquid clusters in pores with the radii $R > R^*$. The liquid flows from such pores in the hydrodynamic time $\tau \sim 10^{-1}$ s. As the pressure is reduced, the quantity R^* decreases and the number of pores from which the liquid flows increases. The volume of the extruded liquid at zero excess pressure is determined by the expression

$$\theta = \int_{R^*}^{\infty} f^V(R)dR. \tag{12}$$

An increase in the temperature results in a decrease in R^*. For this reason, according to Eq. (12), as the temperature is increased, the volume of the liquid extruded until the excess pressure vanishes increases, and, therefore, the volume of the liquid remaining in the porous medium for this time decreases.

The volume of the extruded liquid $1-\theta$ can be estimated from Eq. (12) with R^* given by Eq. (3). The estimates by Eqs. (3) and (12) with the dependence $\sigma(T)$ from [60], as well as $\delta\sigma$ and its temperature dependence determined by the method described in Ref. [51], give $1-\theta(T=277\text{ K}) \sim 0.15$ at temperature $T = 277$ K and $1-\theta(T=289\text{ K}) \sim 0.9$ at temperature $T = 289$ K. These values are close to the experimental values $1-\theta = 0.1$ and 0.8 at time $t = 10$ s, respectively.

It follows from Eqs. (2) and (6) that the character of relaxation of the state formed at the reduction of excess pressure to $p = 0$ is determined by the potential barrier $\delta\epsilon$. According to [61,62], the potential barrier $\delta\sigma$ decreases with an increase in temperature and a decrease in the degree of filling. The value of $\epsilon_{\max}$ at $T = 293$ K and $\theta = 0.1$ is below or about the temperature for all pores. In this case, $\theta < \theta_c$ and only isolated clusters of filled pores are formed in the porous medium. Paths for the extrusion of liquid from these clusters through filled pores are absent. A possible mechanism of the extrusion of liquid from clusters of filled pores in this case can be recondensation.

According to Eq. (11), the relaxation of the formed metastable state occurs through extrusion from local configurations of pores with radii smaller than R^*. The energy barrier for extrusion from these configurations $\epsilon(R,\theta)$ is determined by the interaction between local configurations. Such local configurations are "strongly coupled" with their environment and, therefore, they "interact" with each other. Interacting local configurations of the pore and its environment may be seen as condensed into a metastable state of the entire system of clusters, which decays according to power law (11) with the characteristic time $\tau_q \sim \tau \exp(\frac{\epsilon_{\max}}{T})$, which is $\tau_q \sim 10^5$ s at $\tau \sim 0.1$ s, $\epsilon_{\max} \sim 0.5$ eV, and $T = 277$ K. It follows from Eq. (11) that the exponent α for narrow distributions with the relative width $\frac{\Delta R}{\overline{R}} \sim 0.1$ at these parameters is $\alpha \sim 0.1$.

In view of Eq. (11), the decay of this metastable state is accompanied by a decrease in the degree of filling θ. According to Eq. (3), this results in a decrease in the energy of the interaction between local configurations and, as a result, a decrease in the energy barrier for extrusion $\epsilon(R,\theta)$. As follows from Eq. (11), the quantity $\epsilon_{\max}$ decreases and the exponent α in Eq. (11) increases. For this reason, the decay rate of this metastable state increases with time. According to Eq. (11), the decay of the metastable state begins when the degree of filling $\theta(t)$ is such that $\frac{\Delta R}{\overline{R}} \frac{\epsilon_{\max}}{T} \sim 1$. The decay onset time of the metastable state at $\Delta R/\overline{R} \sim 0.1$, $T = 277$ K, is estimated as $>10^4$ s, in agreement with the experimental data.

The relaxation of the metastable state of interacting local configurations of filled pores continues as long as the percolation cluster of filled pores exists in the system. The existing time of the percolation cluster of filled pores can be estimated from Eq. (11). At $\alpha \sim 0.2$, $\theta_p \sim 0.8$, $\theta_c \sim 0.1$, with allowance for a change in the degree of filling θ in the process of decay of the metastable state, this time is $t_p \sim 10^6$ s. At the degree of filling θ below the percolation threshold, $\theta < \theta_c$, isolated clusters of filled pores are formed in the porous medium. A possible mechanism of extrusion of liquid from such isolated clusters of filled pores can be recondensation, i.e., capillary evaporation and subsequent capillary condensation at the interface between the porous medium and the liquid environment considered in Refs. [52,53,63]. An analysis similar to that used when deriving Eq. (11) gives in this case a logarithmic law of the extrusion of the liquid.

To summarize, the performed analysis shows that there are three stages of the extrusion of the nonwetting liquid from the nanoporous medium. When the pressure is reduced from $p > 200 \times 10^5$ Pa to $p \sim 100 \times 10^5$ Pa, liquid clusters in all filled pores in the water-L23 system should be in states with the extrusion barrier $\delta A \sim 4$ eV. The time of extrusion from such pores is $\tau > 10^{33}$ s. For this reason, the liquid should remain in the porous medium for the time of pressure reduction to 100×10^5 Pa.

When the pressure is reduced to $p < 100 \times 10^5$ Pa, pores appear for which the extrusion barrier δA is negative or can be about the temperature T. The liquid can be extruded from these pores in the hydrodynamic time $\tau_0 \sim 0.1$ s and, therefore, extrusion should be observed for the excess pressure vanishing time $t \sim \tau_p$. As excess pressure vanishes, the number of such pores increases.

At temperatures $T < T_d = 284$ K under the reduction of excess pressure from 100×10^5 Pa to zero in 10 s, the degree of filling decreases from $\theta = 1$ to $\theta > \theta_c$ and the loosely bound state decays with the formation of the initial metastable state of the confined liquid.

The relaxation of the formed metastable state of the confined liquid occurs at times $t = 100$–6000 s according to the power law $\theta(t) \sim t^{-\alpha}$ (11) with the exponent $\alpha \sim 0.1$. At times $t > 10^4$ s, the metastable state decays. In this case, the exponent α increases to $\alpha \sim 0.3$.

The reduction of excess pressure to zero at temperatures $T < T_d = 284$ K results in a decrease in the fraction of the remaining liquid because of the decay of the loosely bound states from $\theta = 1$ to the degrees of filling below the percolation threshold $\theta_c \sim 0.15$. In this case, the relaxation of the system can occur through the evaporation-condensation mechanism, which results in an increase in the characteristic extrusion time of the liquid from the loosely bound states due to both an increase in the extrusion barrier with the temperature and an increase in the transfer time of the Knudsen gas from an evaporated pore to the surface of the granule.

According to Eq. (11), the exponent α depends on the maximum potential barrier and temperature. The exponent α increases with temperature because of a decrease both in the maximum potential barrier $\epsilon_{\max}$ and in the ratio $\epsilon_{\max}/T$. At high temperatures $T > 284$ K, when the excess pressure is reduced to zero, the degree of filling of θ in the time $t \sim \tau_p$ becomes lower than the percolation threshold $\theta_c \sim 0.15$. In this case, the relaxation mechanism of the system changes. The percolation cluster of filled pores disappears, and the extrusion of the liquid occurs through a slower evaporation-condensation mechanism. For this reason, the exponent α at $T > 284$ K should decrease with an increase in the temperature. Thus, an increase in the exponent α with the temperature at $T < T_d = 284$ K due to a decrease in the potential barrier is replaced by its decrease with an increase in the temperature at $T > T_d = 284$ K. This results in the appearance of a maximum in the temperature dependence of the exponent α. This picture corresponds to the experimental data.

ACKNOWLEDGMENTS

This work was performed within the framework of the Center "Physics of nonequilibrium atomic systems and composites" supported by MEPhI Academic Excellence Project (Contract No. 02.a03.21.0005). The reported study was partially supported by RFBR, research projects No. 14-08-00895 and No. 14-08-00805.

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