The law of a stretched exponential and the crossover of the behavior of a disordered nanoporous medium with a non-wetting liquid with its anomalously slow relaxation

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Abstract. Relaxation of a disordered nanoporous medium filled with a nonwetting liquid is studied. An anomalously slow relaxation of the volume of the trapped liquid in such a medium is established, which is characterized by the law of a stretched exponential $\exp[-(t/\tau_0)^\beta]$. At a temperature of $T_c \approx 280$ K, a dispersion transition occurs, namely, the index $\beta$ changes sharply from $\beta > 0.4$ at $T < T_c$ to $\beta < 0.3$ at $T > T_c$. With such a transition, the non-wetting liquid becomes effectively wetting. An explanation for this crossover is proposed as the result of additional jamming of the liquid outflow from the porous medium due to the rupture of the percolation cluster of filled pores, over which liquid escapes.

1. Introduction
One of the general characteristics of disordered systems is their anomalously slow relaxation. These are such systems as granular matter, polymers, metallic glasses, molecular glasses, colloidal media, nanocomposites, etc. The relaxation in such systems is described by Kohlrausch's law (law of a stretched exponential). Namely, the basic property changes with time in accordance with the dependence $\exp[-(t/\tau_0)^\beta]$, where the constant $\tau_0$ denotes the relaxation time and parameter $\beta < 1$, non–exponentiality index or stretching exponent [1,2]. This behavior (jamming) is typical for such media as micellar polycrystals, colloidal fractal gels, surfactant phases, lamellar gels, concentrated emulsions polymeric nanocomposites [3-10], granular material [11], for which the motion from the initial state turns out to be difficult for various reasons in comparison with the usual motion of equilibrium state relaxing systems.

Such jamming is the apparent result of "blockage" or a significant slowdown of the possible motion of the system along part of the path in the configuration space of it is states, which leads to the nonergodic or quasi–nonergodic behavior of such systems [12]. It is thought that, anomalously slow relaxation belongs to the class of cooperative phenomena [3,13-15]. At the present time, several phenomenological models have been proposed for describing anomalously slow relaxation. Their analysis can be found in several recently published reviews [3,13-15]. These models are based on the assumption of the existence of local correlated particle configurations. However, in experiments to measure the correlator of statistical density, they are not recorded.
The disordered nanoporous medium investigated in the present work refers to silica gels that are formed upon a sol–gel transition in a colloidal medium. The random structure of the pores and the frame of the medium "freezes" upon gel formation as a result of a chemical reaction between the colloidal particles. If the pores of the random structure are interconnected, they can be completely filled with liquid. This takes place at porosity values exceeding the percolation threshold, at which an infinite percolation cluster is created in the medium from the associated pores with other pores and thus the pore fluid is filled with the medium. Parameters of the porous medium: the pore size distribution, the specific volume of the pore, and the pore surface, were measured by adsorption-desorption methods of gas [17,18] and liquid porosimetry [19,20,21]. In liquid porosimetry, non-wetting liquid (water) is used, which fills the porous medium at elevated pressure. In this case, the liquid is dispersed and transformed into an ensemble of interacting clusters. The fact of capture of a non-wetting liquid by a random pore structure can serve as a source of properties about a disordered structure. [22-24]. In accordance with [23] and [24] this fact is explained by the effective attraction of clusters. The mutual arrangement of clusters is ultimately determined by correlations in the location of the pores. An abnormally slow relaxation of a liquid captured by a porous medium at times $10^2 < t < 10^5$ was established in [25]. Such a relaxation is observed as a slow flow of liquid from the porous material. The dependence of the degree of filling on time can be approximated by an inverse power law with exponent less than 0.1. With different characteristics of a porous medium non-wetting liquid may not outflow from the porous medium for a several days or even months [26-29]. Small deviations from the critical values of temperature ($T_c$) and degree of filling ($\theta_c$) lead to a dispersion transition (rapid outflow of liquid) [22]. In the present paper it is shown that, in the time range $10^2 < t < 10^5$ s, anomalously slow relaxation of trapped liquid state in a medium with pores of nanometer size is described by the law of a stretched exponential. On this occasion, the exponent ($\beta$) in this law and the relaxation time ($\tau_0$) change discontinuously in the dispersion transition from values $\beta > 0.4$ at $T < T_c$, to values $\beta < 0.3$ at $T > T_c$.

It is presumed that the outflow of liquid can occur only in the presence of bonds between clusters of filled pores. Then, when the percolation cluster breaks, the liquid outflow is jammed.

2. Experiment

2.1. Porous medium

In the experiments, a nanoporous medium, Libersorb 23 (L23), was used. It is a silica gel KSK – G (Large Grain Silica Gel), the disordered pore structure of which is formed as a result of the sol-gel process. The surface of the pores of KSK – G was modified with alkyl silanes to impart hydrophobic properties. Parameters of samples of the porous materials (Libersorb 23) were studied using low-temperature sorption at the Autosorb IQ (Quantachrome, USA) and the helium pycnometer Micro – Ultrapyc 1200e (Quantachrome, USA). The density of the porous medium L23 was $\rho = 1.7798 \pm 0.0016$ g cm$^{-3}$, the specific pore volume $V_p = 0.62 \pm 0.02$ cm$^3$ g$^{-1}$, the porosity of the material was $\phi = 0.52$, the specific surface area $S_p = 199 \pm 7$ m$^2$ g$^{-1}$, the average granule size of the L23 powder was $\sim 10$ μm. The function of the distribution of pores by volume according to the Barrett – Joyner – Halenda (BJH) Analysis is shown in (Figure 1). This function gives only a qualitative representation of the distribution of the pore volume along the radius. The average pore radius is $\langle R \rangle = 5.0 \pm 0.2$, nm in the vicinity of the maximum half – width of the distribution at half – height $\Delta R = 0.4 \pm 0.1$ nm, and the ratio $\Delta R / \langle R \rangle \leq 0.1$. Distribution tails in the region of large and
small pore sizes are also observed. Therefore, due to the smallness of the ratio $\Delta R / \langle R \rangle \ll 1$, the porous medium L23 was used to test the power relaxation model [25]. In such a system (trapped liquid – a fractal infinite percolation cluster of pores), the filled pores form a potential barrier field of local metastable states. It is expected that the relaxation of such states will occur by inverse to the power law.

![Pore size distribution function](image)

**Figure 1.** Pore size distribution function for the porous medium Libersorb 23 by the BJH method.

2.2. **Measurement procedure**

In the experiment, the degree of filling was measured as a function of time. The confined liquid is a liquid that remains in the pores (at the initial state $\theta = 1$) when the total pressure is removed. In this case, the other part of the liquid in the pores rapidly, during the time of pressure decrease, outflow from the pores. For the system L23 – water, the outflow time of this part of the liquid can be less than 1 s [25]. In this paper we have studied the relaxation of a state (slow outflow) of a liquid confined in a porous medium. The scale of the characteristic outflow of the liquid time may differ depending on the mechanism of transport of the liquid through the system of filled pores, or by capillary evaporation and subsequent capillary condensation at the boundary of the bulk liquid and granule of the powder of the porous medium immersed in this liquid. This latter mechanism can work efficiently, obviously, provided that an "infinite" percolation cluster is formed from empty pores, i.e. at the degree of filling of the confined liquid by $0 < \theta_c = 0.85 \div 0.7$. Therefore, the developed technique should provide a measurement of the volume when liquid outflow or when the confined liquid evaporates.

The technique for measuring the volume of a non-wetting liquid system - a porous medium is analogous to the methods of mercury or water porosimetry. It is described in detail in [25]. This technique makes it possible to carry out investigations at temperatures from 243 to 393 K with an accuracy of 0.2 K.
2.3. Results of experiments

Figure 2 shows the experimentally determined values of $\theta$ for different relaxation times $t$ for temperatures $T = 279$ K and 293 K. The experimental values of $\theta$ are obtained by a step–by–step method with two cycles of filling–outflow and a varying time $t$ of observation of relaxation from $t = 10$ s to $t = 10^5$ s at each step. The points in (Figure 2) reflect the results to six measurements $\theta$ for each time $t$. The spread of the values of $\theta$ does not exceed the measurement error. This is evidence that the initial state of the liquid–disordered porous medium system is reproduced when the memory is "erased" (after full filling in the first and second cycles) about the previous states. The coincidence of the values of $\theta$ can be attributed to the fact that after full filling and subsequent removal of excess pressure the system was in one of a large number of degenerate states with the formation of an "infinite" percolation cluster filled at $\theta > \theta_c$ or empty pores at $\theta < \theta_c$. All these states are characterized by the same degree of filling.

![Figure 2. The values of $\theta$ for a different time $t$ show a relaxation for temperatures $T = 279$ K and 289 K.](image)

Between the temperatures $T = 293$ K and 279 K in the water–porous medium L23 system, a dispersion transition occurs when the liquid dispersed in the porous medium becomes metastable with decreasing temperature [22 – 24]. In a narrow region ($\Delta T \approx 10$ K) of temperatures in the vicinity of the critical temperature, the transition occurs adiabatically with increasing temperature from an almost complete non–flow of liquid at $T = 279$ K to an almost complete outflow at $T = 293$ K. It follows from (Figure 2) that in the time interval $60 < t < 6 \cdot 10^3$ s at $T = 279$ K a slow relaxation $\theta(t)$ is observed, and the dependence $\theta(t)$ in the double logarithmic scale within the error margin measurement is described by a straight line. A similar picture is also observed at $T = 293$ K for another gas mechanism of transport and time in the interval $60 < t < 6 \cdot 10^3$ s. However, the slope of the function $\theta(t)$ at this higher temperature is lower, and, consequently, the relaxation rate is smaller in accordance with $T = 293$ K. In Figure 3 shows the dependences of $\theta(t)$ at six temperature values from 277 K to 289 K in the time interval from 13 s to $3 \cdot 10^4$ s. The dependencies presented in Figure 3 can be
described, within the error of measurements, by the law of a stretched exponent, in which the exponent ($\beta$) and the relaxation time ($\tau_0$) are functions of temperature.

**Figure 3.** Dependences of $\theta(t)$ at six temperatures from 277 K to 293 K in the time interval from 13 to $4 \cdot 10^4$ s. (Points – experiment, solid lines – approximation by the function $\sim \exp\left[-(t/\tau_0)^\beta\right]$)

- $T = 277$ K: $\beta = 0.55$, $\tau_0 = 7 \cdot 10^4$ s;
- $T = 279$ K: $\beta = 0.39$, $\tau_0 = 5.5 \cdot 10^4$ s;
- $T = 282$ K: $\beta = 0.07$, $\tau_0 = 1.4 \cdot 10^2$ s;
- $T = 284$ K: $\beta = 0.065$, $\tau_0 = 4 \cdot 10^2$ s;
- $T = 286$ K: $\beta = 0.0053$, $\tau_0 \ll 10^{-10}$ s;
- $T = 289$ K: $\beta = 0.005$, $\tau_0 \ll 10^{-10}$ s

From Figure 4 it follows that with an increase in temperature from 277 K to 279 K, the value of the exponent decreases from values $\beta = 0.55$ to $\beta = 0.39$. A further decrease in temperature by 3 K leads to a significant (by an order of magnitude) change in the parameter to values $\beta = 0.07$. In this case, at a temperature of 282 K, the characteristic relaxation time decreases sharply (by six orders of magnitude) (Figure 5). With a further increase in temperature to 286 K, the parameter $\beta$ falls to values $\beta = 0.0053$ (Figure 4). The relaxation time also decreases by several orders of magnitude (Figure 5). Figure 4 and Figure 5 show the temperature dependence of the parameter and the characteristic relaxation time.
Figure 4. Temperature dependence of the parameter $\beta$ in the law of a stretched exponent $\theta \sim \exp[-(t/\tau_0)^\beta]$.

Figure 5. Dependence on the temperature of the relaxation time in the law of a stretched exponent $\theta \sim \exp[-(t/\tau_0)^\beta]$.
3. Conclusion

Analyzing the results of the experiments (Figures 3-6), it can be stated that after filling the porous medium and then removing the excess pressure, it is possible to realize two different ways of relaxation. At "high" temperatures, \( T > 284 \text{ K} \), almost all the liquid (> 80%) is concentrated in unstable local configurations for which there are flow paths through an infinite cluster of filled pores. As a result, the leakage occurs during the characteristic time of reducing the excess pressure \( t \sim 10 \text{ s} \) (Figure 6).

![Figure 6. Schematic representation of a filled porous medium.](image)

The confined liquid part (with a filling degree less than the percolation threshold \( \theta < \theta_c \)) slowly (at times \( t \gg 10 \text{ s} \)) outflows according to the Kohlrausch law with a small index \( \beta \leq 0.05 \). With this degree of filling, a lower percolation threshold \( \theta_c \), the confined liquid is in unconnected local configurations (Figure 7).

![Figure 7. Schematic representation of a filled porous medium.](image)

These local configurations consist mainly of empty pores, since \( z(1 - \theta_c) \sim z \) (for \( \theta_c \sim 0.1 \)) empty pores are contained in pores of the local configuration (\( z \) – the number of nearest neighbors). Thus, the filled pores of the local configuration turn out to be jammed or "blockage". Therefore, the reduction in the degree of filling can occur according to the following scenario: 1). capillary evaporation 2). diffusion through unfilled pores 3). capillary condensation at the boundary of a porous medium. This leads to a significant slowing down of the relaxation. At temperatures \( T < 282 \text{ K} \), likewise, part of the liquid (< 40%) of the initial volume follows the characteristic time of removal of the excess pressure. However, the majority of the liquid (> 60%) at observation times of the order of \( 3 \times 10^4 \text{ s} \), in accordance with [25], is metastable and slowly relaxes. Relaxation occurs according to the law of a stretched exponential with exponent depending on temperature. Thus, at temperatures \( T \sim 282 \text{ K} \), a crossover occurs in the behavior of the system studied, which is apparently due to the appearance of a dispersion transition in it. This is due to a change in the relaxation
mechanism: due to the jamming of the outflow of liquid after the break of the percolation cluster of the filled pores after the dispersion transition.

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