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Observation of the Anomalously Slow Relaxation of a Nonergodic System of Interacting Liquid Nanoclusters in a Disordered Confinement of a Random Porous Medium

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Abstract

The relaxation of a confined nonwetting liquid dispersed in a disordered nanoporous medium has been experimentally studied in the system consisting of water and the L23 hydrophobized silica gel. It has been found that the relaxation of the system under study is anomalously slow, according to an inverse power law with the exponent $\alpha < 0.16$. It has been also established that the exponent in this law in the temperature range under investigation has a maximum, which can indicate a transition from the regime of the accelerated decay of a quasi-nonergodic state with an increase in the temperature to the regime of the decay of a nonergodic state with its slowing down because of the breaking of paths for the escape of the liquid through the fractal percolation cluster.

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1. Introduction

The disordered system of pores of a random nanoporous medium can be filled with an incompressible liquid at a pressure that can be estimated by the Laplace formula. It was established in [1,2] that, when a certain critical degree

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of filling is achieved and the excess pressure is then removed, a dispersion transition occurs and a part of the liquid can remain in the disordered porous medium. This means that the confined nonwetting liquid is effectively in a wetting state in the form of an ensemble of liquid nanoclusters in the disordered confinement of the porous medium. By varying the degree of preliminary filling of the system of pores, it is possible to change ensembles of pores in the bulk of the random medium in which the liquid is confined [1, 3]. Confinement of the nonwetting liquid is observed as a part of the liquid remaining in the porous medium after its filling [4–10]. As a result of the relaxation process, a transition occurs from the nonergodic metastable state of the ensemble of liquid nanoclusters in pores of the disordered medium to the ergodic state of the empty porous medium immersed in the liquid. The porous medium studied in [1, 2] is a silica gel that is obtained in the sol–gel process of formation of the random medium.

The states and properties of disordered media such as glasses, colloids, polymers, and loose media have been actively studied in recent years [14–24]. In the absence of the consistent inclusion of metastable multiparticle correlations, numerical studies were performed and phenomenological models such as shear transformation zone (STZ), dynamic heterogeneity (DH), and random first order transition theory (RFOT) were introduced and discussed (see, e.g., [13, 17]). These models involve the notion of local structures and are used to describe states and relaxation of glasses, colloids, polymers, and loose media, as well as liquid–glass transitions and sol–gel process, which result in a random order. The state of these media is nonergodic; these media are characterized by the anomalously slow relaxation of nonequilibrium states, which is usually described by a stretched exponential (stretched-exponential relaxation) [14, 18, 24]. Anomalously slow relaxation means that a system cannot reach any point of the phase space in any large observation time [13]. According to [31, 32], such systems are nonergodic. Anomalously slow relaxation is attributed in phenomenological models to the assumed existence and decay of metastable states of random local structures in a disordered medium and to the energy distribution of these states. In the case of metastable states, the characteristic average relaxation time τ is finite, but large. Such states at any large observation time $t < \tau$ can be called quasi-ergodic [31].

Within the consistent statistical description the escape-time distribution of clusters of the confined liquid in pores for the ground state with a fractal percolation cluster was calculated in [3], where a power law of a decrease in the volume of the confined liquid with time was predicted. According to [3], relaxation is a discrete equilibrium process with the overcoming of numerous local maxima appearing because of random local configurations of filled and empty pores with various sizes in the disordered medium. The relaxation of the metastable states of the confined liquid has not yet been studied experimentally, but the anomalously slow escape of a nonwetting liquid from a porous medium, e.g., mercury from porous glass, was sometimes observed [26,27]. The characteristic relaxation (escape) time of a part of the liquid (water in the L23 porous medium) that is not in the confined (metastable) state after filling and removal of excess pressure is 0.1 s at temperatures from 279 to 323 K [29].

In this work, the relaxation of the confined dispersed liquid is observed in the system consisting of water and the L23 hydrophobized silica gel, which is a disordered nanoporous medium. Two metastable states of the dispersed liquid in this system were revealed in [1, 2]. It is found that the relaxation of these states for the system under study is anomalously slow, according to an inverse power law with the exponent $\alpha < 0.16$. It is also established that the exponent in this law in the temperature range under investigation has a maximum, which can indicate a transition from the regime of the accelerated decay of the quasi-nonergodic state with an increase in the temperature to the regime of the decay of the nonergodic state with its slowing down because of the breaking of paths for the escape of the liquid. The observed anomalously slow relaxation of such a system and comparison with the time dependence of the volume of the confined liquid obtained in [3] confirm the correctness of the description of disordered media on the basis of the notion of local metastable structures.

2. Experiments

The nanoporous medium under study was the commercially available KSK-G silica gel with a random structure of pores obtained in the sol–gel process. It was modified in the laboratory headed by Prof. G.V. Lisichkin for obtaining the hydrophobized surface of pores. Using the porometry and pycnometry methods, we determined the parameters of the resulting Libersorb 23 (L23) porous medium: density ρ = 1.7798±0.0016 g/cm^3, specific surface area of pores S = 212±7 m^2/g, and specific volume of pores v = 0.62±0.02 cm^3/g. The pore size distribution appeared to be close to a Gaussian distribution with the mean radius $\bar{R}$ = 5.0±0.2 nm and the relative FWHM