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Anomalously slow relaxation of the system of liquid clusters in a disordered nanoporous medium according to the self-organized criticality scenario

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ABSTRACT

We propose a physical model of a relaxation of states of clusters of nonwetting liquid confined in a random nanoporous medium. The relaxation is occurred by the self-organized criticality (SOC) scenario. Process is characterized by waiting for fluctuation necessary for overcoming of a local energy barrier with the subsequent avalanche hydrodynamic extrusion of the liquid by surface forces of the nonwetting frame. The dependence of the interaction between local configurations on the number of filled pores belonging to the infinite percolation cluster of filled pores serves as an internal feedback initiating the SOC process. The calculations give a power-law time dependence of the relative volume θ of the confined liquid $\theta \sim t^{-\nu}$ ($\nu \sim 0.2$) as in the picture of relaxation in the mean field approximation. The model of the relaxation of the porous medium with the nonwetting liquid demonstrates possible mechanisms and scenarios of SOC for relaxation of other disordered systems.

1. Introduction

It is known that anomalously slow relaxation and hysteresis properties are characteristic phenomena of many disordered media [1–4]. These media include atomic, molecular and polymeric glass of atomic particle size, colloid media, nanocomposites with nanoscale particles and loose material with a micron scale particles, as well as spin glasses. The phenomenon of hysteresis is associated with the existence of long-lived metastable states and related spatial inhomogeneity of a disordered medium. The assumption of the existence of heterogeneous inhomogeneities and local configurations is central in phenomenological models of description of anomalously slow relaxation in disordered media. Analysis of these models is performed in several recent reviews [1,2,5,6]. From this analysis it follows that the cause of the inhomogeneity of disordered media, and therefore the mechanism of anomalously slow relaxation are unclear until today.

Anomalously slow relaxation and hysteresis are also characteristic properties of a system of nonwetting liquid–disordered nanoporous medium. In this work we discuss the new mechanism of formation of a local configurations and anomalously slow relaxation of the liquid clusters in a disordered nanoporous medium. Anomalously slow relaxation was found in [7,8] for a system of water–disordered hydrophobized nanoporous medium Libersorb-23 (L23) and Fluca 100C8.

If a pressure exceeds a certain critical value which can be estimated by the Laplace equation, then hydrophobized porous medium can be filled with liquid. At intrusion liquid in porous medium is dispersed and becomes a system of clusters in confinement. Hysteresis of intrusion–extrusion is observed for many porous media, water, liquid metals, and aqueous salt solutions [9–16]. Hysteresis was observed for disordered nanoporous medium at adsorption–desorption of gases [16,17].

As it was observed in [7,8] the part of liquid can be quickly extruded from nanoporous medium and the state of the rest part of liquid confined in a disordered pore structure then slowly relaxes by extrusion so that the degree of filling of the porous medium θ is changing with time according to a power law $\theta \sim t^{-\nu}$, $\nu \approx 0.2$. Depending on the properties of the porous medium, nonwetting liquids can remain in it for many days and even months [16–18]. This effect was observed for nanoporous media with the porosity above the percolation threshold so that a percolation cluster of filled with liquid pores appeared in the porous medium and the fast hydrodynamic outflow of the nonwetting liquid through this cluster was possible but was not observed experimentally.

The confinement of liquid in accordance with the [19] associated with the effective interaction (attraction) clusters in neigh-

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boring pores. The energy of this interaction is calculated as the difference between the surface energies of the two clusters in the neighboring connected pores compared to the surface energy of individual clusters. Previously, such cooperation was taken into account in [20] at the description of the thermal effects in intrusion–extrusion nonwetting liquid from a disordered porous medium, and depending of the fraction of the confinement nonwetting liquid on the observation time [16].

A system of liquid clusters is a nonlinear dissipative systems. The relaxation of such system can be considered in the frameworks of model of self-organized criticality (SOC) [21,22]. This model was proposed in [23,24] to describe relaxation as an avalanche process of falling of a pile of sand. It is commonly accepted [21, 22] that the SOC state appears in nonlinear dissipative systems in the critical state that relax without the external control parameter through rapid avalanche transitions between different metastable states of a system. The critical state is maintained not at a point, but in a wide region of the phase diagram of states through a nonlinear feedback mechanism because of the existence of the internal mechanism leading to the dynamic self-organization of transitions between intermediate metastable states of the system. Self-organized criticality is characteristic of the systems with fractal objects. However, physical mechanisms responsible for avalanche transitions between metastable states, as well as the reason for the appearance of the feedback mechanism leading to the dynamic self-organization of transitions between such states, are not yet understood. In particular, numerical studies [25] indicate that the properties of SOC with avalanche relaxation for spin-glass systems are not manifested at a finite number of neighbors and a divergent number of neighboring interacting spins are necessary.

In this work, we propose a new mechanism of anomalous relaxation of states of a dispersed liquid confined in a random nanoporous medium, which can be characterized as the SOC mechanism in revealed properties. In contrast to the description of relaxation in the mean-field approximation, the relaxation of state of disordered medium filled with the nonwetting liquid is represented in this case as evolution of an inhomogeneous state of interacting local metastable configurations of liquid clusters. The relaxation of local metastable configurations results in an anomalously slow relaxation of the nonwetting liquid confined in the nanoporous medium.

2. Main part

Let us first discuss the characteristic time for changes in the state system consisting of nanoporous medium filled with nonwetting liquid. After intrusion at excess pressure and removal of excess pressure, a part of the liquid can be in an unstable state and be removed in a hydrodynamic time through filled pores of the infinite percolation cluster [8]. The performed experiments showed that, for the L23 hydrophobized silica gel, where the average radius of pores is $\bar{R} = 4$ nm and the size of granules is 10 microns, immersed in water and filled with water at excess pressure sufficient for filling of pores with the minimum size, the hydrodynamic time of outflow of the entire liquid was $\tau_0 \sim 1$ s [19,26]. Another part of the liquid is in a spatially inhomogeneous state confined in the disordered structure.

It was shown in [26] that the relaxation of the metastable state in the L23–water system occurs at times $t_0 \sim 10^5$ s much larger than the thermal equilibrium establishment time $\tau_e \sim 1$ s and the hydrodynamic extrusion time $t_0 \gg \tau_0,\ \tau_e$. These time relations allow us to describe such a nonequilibrium state of the disordered medium with the confined liquid and its relaxation at times $t \sim t_0 \sim 10^5$ s by local equilibrium distribution functions in $5N$-dimensional phase space of pores coordinates, pore radii and their occupation numbers n_i of all N pores [19,26,8].

A change of the system energy at the extrusion liquid from the one pore can be reduced to the energy $\delta\varepsilon_n$ of the local configuration of the pore and its environment [19]. The detailed implementation of the reported sequence of calculations is given in [8]. The calculations provide the result corresponding to the quasiparticle approximation [27].

Within the framework of the approximations using pair distribution function of the model randomly distributed spheres of different sizes (RDS) [28,29], the change in energy $\delta\varepsilon_n$ of the local configuration containing n empty pores round the depleted pore can be represented as in [19]:

$$\delta\varepsilon_n = -4\pi R^2 \delta\sigma\,(1-\eta) + 4\pi R^2 \eta\sigma\,(1-\theta)^n P(\theta)^{z-n} \frac{z-2n}{z} \frac{z!}{n!(z-n)!} \tag{1}$$

Here, σ is the surface energy of the liquid, $\delta\sigma = (\sigma_{ls} - \sigma_{sg})$ is the difference between the surface energies of the solid–liquid and solid–gas interfaces, $P(\theta)$ is the probability for the pore to belong to the infinite cluster of filled pores (monotonic function of the degree of filling θ), $\eta = q\left(\frac{R_0}{R}\right)^{\alpha}$ accordance to the model of RDS [28], the parameter is $q(\varphi) \sim 1$ and depends on porosity φ and R_0 is the minimum pore radius in a porous medium, which is determined by the pore radius distribution function and, on the order of magnitude, is the average pore radius divided by the average number of the nearest neighbors ($R_0 \sim R/z$). A value α is an exponent above zero, which depends on the pore size distribution. It reflects a decrease of fraction of meniscus surface relative to the entire surface of pore with the increasing of pore size [19,26]. In accordance with the Eq. (1) the energy of the nth local configuration depends on the degree of filling θ, the radius of the pore R and number of nearest neighbors z. Dependence $\delta\varepsilon_n$ on θ considers the interaction of the local configurations through a field of infinite percolation fractal clusters of filled pores.

A positive $\delta\varepsilon_n$ value means the existence of an energy barrier for the decay of the metastable state of the configuration. According to Eq. (1), there are local minima and maxima of the energy necessary for the outflow of the liquid from the nth local configuration. Thus, beyond the mean-field approximation, the inhomogeneous state, because of the dependence of $\delta\varepsilon_n$ on the degree of filling, consists of interacting local configurations each in the metastable state with the energy $\delta\varepsilon_n$. The outflow of the liquid from the inhomogeneous state of the porous medium, which contains metastable local configurations, occurs through the mechanism of the dissipative transport of the liquid through the percolation cluster of filled pores. Since the degree of filling θ of the porous medium with the liquid varies as the liquid is removed; i.e., the percolation cluster of filled pores decreases, it follows from Eq. (1) that the state of metastable local configurations changes nonlinearly. Therefore, the relaxing system of liquid clusters in confinement is a nonlinear nonequilibrium dissipative system.

The time of relaxation τ_n is given by the expression [30]:

$$\tau_n = \tau_0 \exp(\delta\varepsilon_n(R,\theta,T)/T) \tag{2}$$

According to Eq. (2), the relaxation time τ_n of the nth configuration is determined by the waiting time $\sim \exp(\delta\varepsilon_n(R,\theta,T)/T)$ of a fluctuation necessary for overcoming the local barrier $\delta\varepsilon_n(R,\theta,T)$ and the time τ_0 of the subsequent barrierless hydrodynamic outflow of the liquid from the local configuration. It follows from Eq. (2) that the quantity $\delta\varepsilon_n(R,\theta,T)$ serving as the barrier of the nth local configuration depends on the pore radius, probability $P(\theta)$ of belonging to the percolation cluster, degree of filling θ, and, hence, according to Eq. (1), depends on the interaction between local configurations in the percolation cluster. At the outflow of the liquid and the decay of the nth metastable state, the