

Scenario SOC abnormally slow relaxation of the system clusters the fluid in disordered nanoporous confinement environment

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Abstract. The relaxation of the system of the nanoporous medium with the nonwetting liquid is a self-organized criticality process characterized by waiting for fluctuation necessary for overcoming a barrier of local metastable state with the subsequent avalanche decay of local metastable configurations of pores. 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.

1. Introduction

Anomalous slow relaxation and hysteresis properties are a 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 performed in several recent reviews [1,2,5,6]. From this analysis it follows that the cause of the inhomogeneous of disordered media, and therefore the mechanism of anomalously slow relaxation are unclear until today.

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) [7,8]. This model was proposed in [9,10] to describe relaxation as an avalanche process of falling of a pile of sand. It is commonly accepted [7,8] 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 [11] 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 liquid confined in a random nanoporous medium, which can be characterized as the SOC mechanism in revealed properties. The interaction energy of a system of clusters is calculated in the quasiparticle approach [12] as the sum of the energies of the local liquid cluster configurations interacting with clusters in neighboring pores. The process of relaxation involves overcoming the metastable state of the local configurations and the subsequent rapid hydrodynamic extrusion of the liquid. 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 of the density of states and extrusion time distribution functions of liquid clusters give a power-law time dependence of the relative volume θ of the confined liquid $\theta \sim t^{-\nu}$ ($\nu \sim 0.1$). Such a dependence is characteristic of known self-organized criticality phenomena.

2. Main part

We assume that the disordered nanoporous medium includes pores with different sizes and the size of the porous medium is much larger than the maximum size of pores, so that the porous medium can be considered as infinite and the infinite percolation cluster of empty pores is formed in it.

According to [13,14], the metastable state of filled pores in the porous medium is formed at times $t > \tau_0$, relaxes slowly at times much larger than τ_0 , and then decays at times $t > t_0$. It was shown in [35] that the relaxation of the metastable state in the Libersorb23–water system with a narrow pore size distribution with the relative width $\Delta R / \bar{R} < 0.1$ occurs at times $t_0 \sim 10^5$ s much larger than the thermal equilibrium establishment time $\tau_e < \tau_0$ at the extrusion of the liquid from the pore $t_0 \gg \tau_0, \tau_e$. Therefore, such a state of the disordered porous medium with the confined nonwetting liquid can be described by local equilibrium distribution functions and can be considered thermodynamically with distribution functions in $5N$ -dimensional phase space of pores coordinates, pore radii and their occupation numbers n_i of all N pores in the porous medium [13-15]. For the filling of pores in the porous medium, it should contain an infinite cluster through which the transport of the liquid is possible [13,14]. Consequently, the percolation cluster of filled pores is formed inside this percolation cluster of pores at filling [13]. It follows that the ground state of partially filled porous medium is a state containing a percolation cluster of pores with the percolation cluster of filled pores the inside of it.

The state of the system containing the infinite cluster of filled pores can have many realizations; i.e., this state is degenerate. Consequently, this state can be characterized by the probability $P(\theta)$ for the pore to belong to the infinite cluster of filled pores.

The liquid is removed from pores of porous medium only if at least one of its neighboring pores belongs to the infinite cluster of filled pores through which the extrusion of the liquid from a granule of the porous medium is possible. According to [13-15] a change in the complete thermodynamic potential, i.e., the energy of the porous medium filled to the degree of filling θ , at extrusion of liquid from pores in the case of small changes of the degree of filling θ can be represented in the form of the sum of the energies $\delta\mathcal{E}(\vec{r}_1, R_1, \theta)$ of local metastable configurations of a pore and its environment. This energy is the sum of the change of energy $\delta\mathcal{E}(r_1, R_1, \theta)$ of the interface between the porous medium and liquid and the energy $\delta\mathcal{E}_{int}(\vec{r}_1, R_1, \theta)$ necessary for the formation of menisci in the throats of the neighboring pores, which is proportional to the difference between the amount of meniscus before and after emptying pores per nearest neighbor. This quantity can be treated as the energy of the interaction $\delta\mathcal{E}_{int}$ of the liquid cluster in the pore with a liquid cluster in neighboring pores. Since the extrusion of liquid occurs through percolation cluster of filled pores, the energy $\delta\mathcal{E}_{int}(\vec{r}_1, R_1, \theta)$ can be

characterized by the probability $P(\theta)$ for the pore to belong to the infinite cluster of filled pores and depends on the number of nearest neighbors z of depleted pore and the number of unfilled pores in its environment, composing the local configuration of depleted pore.

It was shown in [13-15] that a change in energy $\delta\mathcal{E}$ of pore at the extrusion of the liquid from this pore can be represented as a sum of changes in energy of various local configurations containing n empty pores $\delta\mathcal{E}_n$, divided by the number of nearest neighbors [13,14]

$$\delta\mathcal{E}(\theta, R) = \frac{1}{z} \sum_{n=0}^{z-1} \delta\mathcal{E}_n, \quad (1)$$

Expression for the energy $\delta\mathcal{E}_n$ of the local configuration containing n empty pores was obtained in [13,14]:

$$\delta\mathcal{E}_n = -4\pi R^2 \delta\sigma \left(1 - q \left(\frac{R_0}{R}\right)^\alpha\right) + 4\pi q R^{2-\alpha} R_0^\alpha \sigma (1-\theta)^n (P(\theta))^{z-n} \frac{z-2n}{z} \frac{z!}{n!(z-n)!} \quad (2)$$

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), $R_0 \sim \bar{R}/z$ is the minimum radius in the pore size distribution, $\alpha \approx 0.3$, and $q \sim 1$ [13,14]. The relative number of filled pores in the configuration can be estimated from the relation $z-n \sim \theta$. Therefore, as follows from Eq. (2) $\delta\mathcal{E}_n$ at a given degree of filling θ can be both positive and negative, depending on the number n . A negative $\delta\mathcal{E}_n$ value means that the extrusion of the liquid from pores in the n th state is energetically favorable. A positive $\delta\mathcal{E}_n$ value means the existence of the energy barrier for the decay of metastable configurations. Thus, Eq. (1,2) indicates the existence of local maxima and minima of the energy necessary for the extrusion of the liquid from the n th state. We now calculate the density of states $g(E, \theta)$ corresponding to the presence of the local configuration in a state with the energy E at the degree of filling θ :

$$g(E, \theta) = \int_0^\infty dR \sum_{n=0}^{z-1} \delta(E - \delta\mathcal{E}_n(R)) f(R). \quad (3)$$

Figure 1 shows the energy dependence of the density of states of the local configuration for various degrees of filling θ . The calculations were performed with the results for the surface tension coefficient $\sigma(T)$ from [16]. The surface tension coefficient at $T = 293$ K is 75 mJ/m^2 [17]. The $\delta\sigma$ value at $T = 293$ K is 22 mJ/m^2 . The quantity $R_0 \sim \frac{\bar{R}}{z}$ was estimated within the model of randomly distributed spheres [17,18].

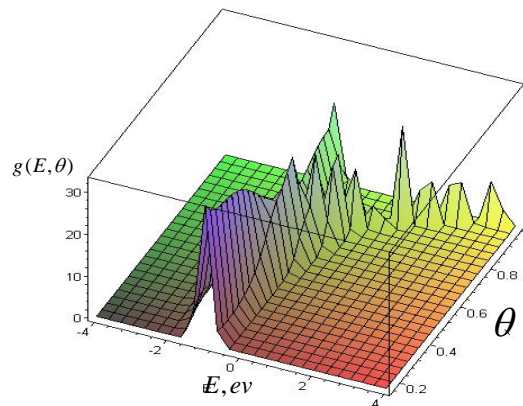


Figure 1. Density of states of the local configuration versus the energy and degree of filling of the medium θ .

It is seen in Fig. 1 that the states of the system at the degree of filling $\theta = 0.5$ are concentrated at negative energies of local configurations $E < 0$ or at energies below the temperature $E < T$. The characteristic liquid extrusion time τ for these states is determined by the hydrodynamic time τ_0 of the motion of the liquid in the porous medium. At the degree of filling $\theta = 0.7$, some local configurations are in states with a negative energy. The liquid flows out of these configurations in the hydrodynamic time. The other part of the liquid is in a state for which the potential barrier is positive and amounts $E \sim 1 \text{ eV}$. The characteristic liquid extrusion time for these states is determined by the potential barrier for extrusion and can significantly exceed the hydrodynamic time, $\tau \gg \tau_0$, when the barrier is above the temperature, i.e., $\delta A > T$. These configurations correspond to a metastable state of the liquid with the decay time determined by the barrier. At the degree of filling $\theta = 0.8$, the number of local configurations with a negative energy $E < 0$ decreases, whereas the number of local configurations with a positive barrier increases. At the same time, states with a higher barrier, $E > 1.5 \text{ eV}$, appear in addition to states with $E \sim 1 \text{ eV}$. These configurations correspond to the appearance of additional metastable states of the liquid with a longer decay time, which is determined by the height of the barrier.

From the analysis made above follows that the extrusion of the liquid from different local configurations of pores can take different times, and the number of configurations of pores involved in extrusion depends on the observation time. As a result, the state of the system relaxes and the amount of the liquid remaining in the porous medium $\theta(t)$ depends on the observation time.

To calculate this dependence following [13,14] can be done by the distribution function $F^V(t)$ for the extrusion times from a pore with the radius R and volume $V = (4\pi/3)R^3$, using the relaxation time

$$\tau_n = \tau_0 \exp(\delta \varepsilon_n(R, \theta, T)/T). \quad (4)$$

It follows from Eq. (6) that the relaxation time τ_n of the n th configuration is determined by the waiting time of fluctuation $\sim \exp(\delta \varepsilon_n(R, \theta, T)/T)$ necessary for overcoming the local barrier $\delta \varepsilon_n(R, \theta, T)$ and by the time τ_0 of the subsequent barrierless hydrodynamic extrusion of the liquid from the local configuration. According to Eq. (6), the quantity $\delta \varepsilon_n(R, \theta, T)$ serving as the barrier for the n th local configuration depends on the radius of the pores, the probability of belonging to the percolation cluster $P(\theta)$, and the degree of filling θ of the porous medium with the liquid and, thereby, according to Eq. (1,2), it depends on the interaction between local configurations in the

percolation cluster. At extrusion of liquid and the decay of the n th metastable state is accompanied by a decrease in the number of filled pores in the percolation cluster and, hence, in the number of neighboring pores. Therefore, the energy of the multiparticle interaction in Eq. (1,2), as well as thereby the lifetime of local configurations with different numbers n , decreases. As a result, the decay of the n th local metastable configuration reduces the decay time of local metastable configurations with different numbers n and with different, initially higher energy. In this case, 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 at the decay of metastable states in a wide region of the degree of filling $\theta > \theta_c$, where θ_c is the percolation threshold.

As follows from Eq. (1,2), the volume fraction $\theta(t)$ of pores from which the liquid is not extruded can be represented in the form

$$\theta(t) = \sum \theta_n(t), \theta_n(t) \sim \theta_{np} \left(\frac{\tau_{qn}}{t} \right)^{a_n}, a_n = \frac{1}{1 + (2 - \alpha) \frac{\Delta R}{R} \frac{\varepsilon_{n\max}}{T}}, \quad (5)$$

$$\tau_{qn} \sim \tau_0 \exp\left(\frac{\varepsilon_{n\max}}{T}\right), \theta_{np} \sim \theta \int_0^\infty \eta(\delta\varepsilon_n(R)) dR f^V(R).$$

where $\varepsilon_{n\max} = \max \delta\varepsilon_n$ is the maximum energy barrier for the decay of the local metastable configuration in the n th state.

As follows from Eqs. (5), the exponents a_n and times τ_{qn} specify the relaxation law of the state of the n th local configuration, are determined by the energy barrier $\varepsilon_{n\max}$. The volume fraction of the liquid remaining in the local metastable configuration in the n th state decreases according to a power law with the exponent a_n and characteristic time $\tau_{qn} \sim \tau_0 \exp\left(\frac{\varepsilon_{n\max}}{T}\right)$. According to Eqs. (5), different states $\theta_n(t)$ relax with different characteristic times τ_{qn} and different exponents a_n . The slowest relaxing state of the local configuration corresponds to $\tau_{qn} = \max$ and $a_n = \min$ and, hence, $\varepsilon_{n\max} = \max$; whereas the slowest relaxing state to $\tau_{qn} = \min$ and $a_n = \max$ and, therefore, $\varepsilon_{n\max} = \min$.

It follows from Eq. (5) that the decay of the local metastable configuration in the n th state results in the disappearance of the corresponding term in sum (5) and, consequently, in a decrease in the degree of filling θ . As a result, according to Eq. (1,2), the energy of the interaction between local configurations decreases and, therefore, the energy barrier $\delta\varepsilon_m(\theta)$ for extrusion from other states changes. For this reason, according to Eqs. (1,2), the volume fraction of the liquid remaining in the metastable state in the porous medium should be determined from the self-consistent equation

$$\theta(t) = \sum_{n=0}^{z-1} \theta_{np}(\theta(t)) \left(\frac{\tau_{qn}(\theta(t))}{t} \right)^{a_n(\theta(t))}. \quad (6)$$

To analyze this equation, we note that the terms in sum (9) include different exponents $a_n(\theta(t))$ and times $\tau_{qn}(\theta(t))$. As a result, the relaxation of the system determined by the dependence $\theta(t)$ at each time instant occurs as the «rapid» relaxation of the n th state, which is determined by the maximum exponent a_n and the minimum time τ_{qn} , and as the «slow» relaxation of the n th current state, which is determined by the minimum exponent a_n and the maximum time τ_{qn} . According to Eq. (6), the set of such modes contributes to the total relaxation of the metastable state at times $t \sim t_0$

$\gg \tau_0$. Therefore, the relaxation of the metastable state in times $\tau_0 \ll t \sim t_0$ corresponds to «the trajectory of motion» of the system in the (θ, n) space with the slowest relaxation of the local metastable configurations in the n th states. The relaxation of the state of the local metastable configurations on this trajectory occurs because of feedback with the minimum exponent a_n and maximum time τ_{qn} . Figure 2 shows the energy of the state of the local configuration $\delta\epsilon_n$ corresponding to the n th mode for the configuration of the pore with the radius equal to the average radius $R = \bar{R}$ for a Gaussian pore volume distribution $f^V(R)$. The calculations were performed with the same parameters as for Fig. 1.

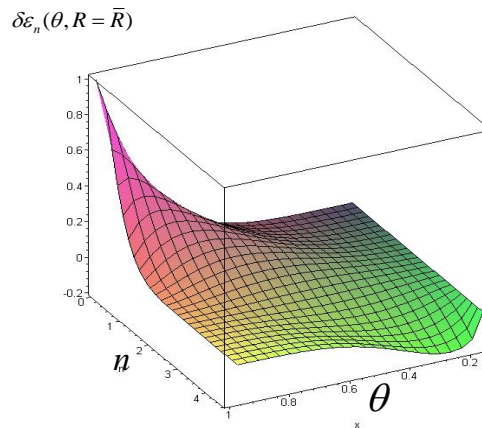


Figure 2. Energy of the state of the local configuration $\delta\epsilon_n$ corresponding to the n th mode for the configuration of the pore with the radius equal to the average radius $R = \bar{R}$ for a Gaussian pore volume distribution $f^V(R)$. The states on the crest correspond to the critical state of the system.

It is seen in Fig. 2 that the energy of the state of the local configuration $\delta\epsilon_n$ as a function of the variables θ, n has a maximum (crest) corresponding to the states and degrees of filling of local metastable configuration with the slowest relaxation. Consequently, the states on the crest determine the critical state of the system throughout the range $\theta > \theta_c$. According to Eq. (6), the time dependence of the degree of filling for the critical state is given by the expression

$$\theta(t) \approx \theta_{n(\theta(t))p}(\theta(t)) \left(\frac{\tau_{qn(\theta(t))}(\theta(t))}{t} \right)^{a_{n(\theta(t))}(\theta(t))}. \quad (7)$$

Here, $n(\theta(t))$ is the number corresponding to the state of the local configuration on the slowest relaxing trajectory (critical state).

Expressions (7) describe the relaxation of the formed metastable state corresponding to the mean-field picture considered in [20]. According to [15], the formed metastable state corresponding to bound states of interacting local configurations of filled pores relaxes slowly according to a power law with the exponent a given in Eqs. (10) in times $t \sim \tau_q$. The formed metastable state decays at times $t > t_0$ because of a decrease in the degree of filling θ and, as a result, a decrease in the energy barrier for extrusion $\mathcal{E}(R, \theta_1)$. In this case, the \mathcal{E}_c value decreases and the exponent a increases according to Eqs. (7). Consequently, the decay rate of the metastable state increases with the relaxation of the system.

The final expressions indicate that the relaxation of the system occurs through the decay of the local metastable configuration responsible for the formation of critical conditions for the decay of other local metastable configurations with a different, initially higher energy. The decay of the metastable state of some local configurations reduces the number of filled pores in this percolation cluster and, therefore, the number of neighboring pores. As a result, the energy of the multiparticle interaction decreases and critical conditions appear for the decay of other metastable configurations. In this case, the system relaxes on the trajectory in the (configuration number, degree of filling) space corresponding to the critical state with the slowest relaxing mode. The time dependence of the relative volume θ of the confined liquid on this trajectory has the form of a power law given by Eq. (7)) (Figure 3) Figure 3 shows a relaxation picture in approach of an average field [20].

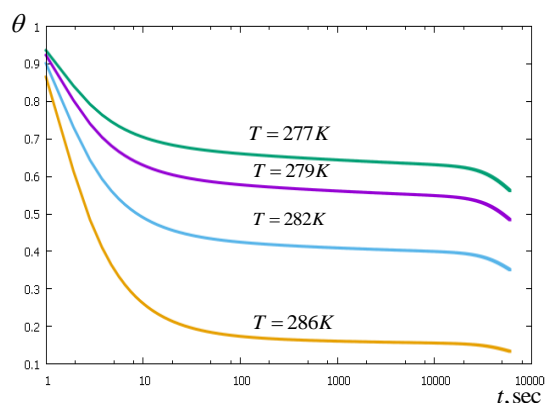


Figure 3. Qualitative depending of the volume fraction remaining liquid on time at different temperatures.

From Fig. 3 it is seen that the relaxation of the formed metastable state of confinement liquid occurs at times $t = 100\text{--}6000\text{s}$ according to a power law $\theta(t) \sim t^{-\alpha}$ (18) with $\alpha \sim 0.1$. At times $t > 10^5$ s metastable state decays.

Conclusion

To summarize, the relaxation of the system of the nanoporous medium with the nonwetting liquid is a self-organized criticality process characterized by waiting for fluctuation necessary for overcoming a barrier of local metastable state with the subsequent avalanche decay of local metastable configurations of pores. 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 model of the relaxation of the porous medium with the nonwetting liquid developed in this work demonstrates possible mechanisms and scenarios of SOC for disordered atomic systems.

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