

Applying a cellular automaton model to describing the anomalous relaxation of the metastable states in the disordered porous media

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Abstract. We propose a numerical model of outflow of the nonwetting liquid from previously completely filled nanoporous media based on cellular automata theory. It was shown that the relaxation of this system has an avalanche-like behaviour, which is inherent to phenomenon of self-organized criticality (SOC). Avalanche size and energy distributions were obtained. It was found that spectra have a typical for SOC theory power-law dependence $N(s) \sim s^{-\beta}$ with $\beta = 2.73$, and $N(E) \sim E^{-\beta_{en}}$ with $\beta_{en} = 2.25$.

1. Introduction

In paper [1, 2] anomalously slow (power-law) relaxation of the system “disordered nanoporous media – nonwetting liquid”, when $\theta \sim t^{-\alpha}$ ($0 < \alpha < 0.2$), was observed. Based on that, in [3, 4] it was assumed that in this kind of systems self-organized criticality, where power-law relaxation is typical, is possible. This model first proposed by Bak to describe relaxation of “sandpile” system [5, 6]. It was shown in [5, 6] that after critical angle is reached further relaxation happens through avalanche-like transitions between different metastable states of a system, moreover avalanches have a power-law size distribution $N(s) \sim s^{-\beta}$. Later it became clear that this mechanism is characteristic of the whole class of systems in the critical state with common features: they are all non-linear, open and dissipative [7]. The critical state is maintained in a wide region of the phase diagram through the feedback mechanism. Such properties make the mathematical description of the relaxation process a very difficult problem [8], there are only limited number of models, which can be exactly solved. One of the main tools in the study of systems that are capable of self-organized criticality is numerical simulation, using cellular automata theory [9]. In this model evolution of the system in time is described by a discrete way (iteratively), and the system is defined as cellular structure. Each cell on grid is on some state that corresponds to certain state of the element in simulated system. To use the model initial condition and rules of transition between states are required. The advantage of this model is that information about local mechanisms “is not lost” with this approach. It is especially important in modelling processes in disordered systems, where the dynamics of local configurations plays crucial role in relaxation of the metastable states [10].

In [3, 4] feedback mechanism, by which SOC can be implemented in such systems, was proposed. It was shown that the interaction between local configurations depends on the relative



volume θ of the confined liquid. In other words, liquid volume change leads to shift of the energy barriers spectrum to lower values, resulting formation of critical conditions for other metastable states. According to the above, decay of the metastable states in systems of nonwetting liquid – disordered nanoporous media is considered as cooperative process with long-range correlations. Besides, there was also mentioned a local mechanism, whereby maintaining the system in critical state occurs due to change of the energy barriers in local configuration of pore after its emptying.

Numerical experiment could help to verify the idea of SOC scenario for relaxation in system of nonwetting liquid in disordered nanoporous media. This approach allows to look at the process “from the inside”, based on the basic mechanisms of the system relaxation. Moreover, numerical simulation allows to get data about the characteristics, which are unmeasurable in real experiment, such as avalanche size distribution or energy barriers spectrum of the metastable configurations in the system. Namely, power-law distribution of the avalanches in relaxation process could be a substantial argument in favour of presence of self-organized criticality in such systems. This paper is dedicated to consideration of using cellular automata model in simulating “nonwetting liquid – nanoporous media” systems’ relaxation process.

2. Main part

Herein, porous material is considered within the framework of the model of randomly distributed polydisperse overlapping spheres [11]. Let a system has a cubic form with side L . Then, if $L \gg \bar{R}$ [12]:

$$\varphi = 1 - \exp(-\eta) \quad (1)$$

Here, φ is the porosity of system, $\eta = \frac{N}{L^3} 4\pi \int f(R)R^2 dR$, $f(R)$ is the probability density function of the radii.

Offered results were obtained for the system with $L = 50 \bar{R}$, so the condition $L \gg \bar{R}$ can be regarded as fulfilled. Then, setting $f(R)$, L and φ and using (1), we can get number of pores N corresponding to given system.

In this paper, outflow of the nonwetting liquid from previously completely filled nanoporous media was studied. Besides, initially filled with liquid only the part of the system that belongs to percolation cluster of empty pores. Relaxation of this subsystem will be discussed further. The external pressure is removed linearly from p_{max} to p_{min} by the time T_p .

Conditions of the outflow of a liquid from a pore is determined based on statistical theory of fluctuations. We can write isothermal work for liquid outflow as:

$$\delta A = pV + \sigma_{lg}(S_{neut} - S_{lg}) - (\sigma_{ls} - \sigma_{gs})S_{ls} = pV + \sigma \delta S - \delta \sigma S, \quad (2)$$

here, p – external pressure, V – volume, available for liquid outflow from pore; σ_{lg} – relative surface energy of the liquid–gas; σ_{gs} – relative surface energy of the gas–solid; σ_{ls} – relative surface energy of the liquid–solid; S_{neut} – area of the “neutral surface” that changes from “liquid–liquid” to “liquid–gas” after the outflow of liquid occurs; S_{lg} – area of the “liquid–gas” menisci; S_{ls} – area of the “liquid–solid” surface.

The probability of “filled pore – empty pore” transition, according to the statistical theory of fluctuations, is then given by:

$$\omega \sim \exp\left(-\frac{\delta A}{T}\right) \quad (3)$$

If we now assume that only two states of pore are possible – filled and empty, – then from normalization condition it follows that outflow probability is:

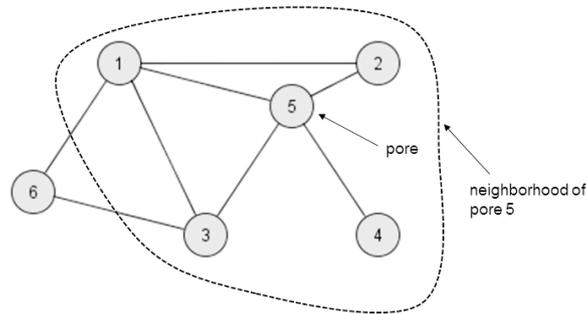


Figure 1. The system as a graph

$$\omega = \frac{\exp\left(-\frac{\delta A}{T}\right)}{1 + \exp\left(-\frac{\delta A}{T}\right)} = \frac{1}{1 + \exp\left(\frac{\delta A}{T}\right)} \quad (4)$$

It is obvious that after the liquid is extruded from the pore the “liquid – gas” surface area increases for pores of its local configuration, therefore their energy barriers for outflow are decreased. This causes a feedback mechanism, by which the system is maintained in critical state, and avalanche-like evolution becomes possible, when outflow from one pore leads to chain of decays of metastable states in some region.

Assuming that $\bar{R} \sim 1 \text{ nm}$, $\sigma \sim 10^2 \frac{\text{mJ}}{\text{m}^2}$, we can estimate the value of the energy barrier for outflow:

$$\delta A \sim \sigma R^2 \sim 10^{-18} \cdot 10^2 \cdot 10^{-3} \text{ J} \sim 1 \text{ eV} \sim 10^4 \text{ K} \quad (5)$$

It follows from (5) that for systems with a pores of nanometre size characteristic value of the energy barrier is much bigger than the temperature $T \sim 300 \text{ K}$. Thus, if $\delta A < 0$, then the outflow probability $\omega \approx 1$, therefore it can be assumed that the outflow occurs guaranteed in this case.

In accordance with (2), for the calculation of work for liquid outflow the values of V , S_{neut} , S_{lg} and S_{ls} for pore are needed. In this paper, intersections of more than three spheres are not regarded, so every local configuration was considered as a set of double and triple intersections. All these cases were completely analysed in [13, 14, 15].

It is now possible to turn to a discussion of a cellular automaton for the “nonwetting liquid – nanoporous media” system. Evolution of the system in this model is described in a discrete way, therefore for an adequate simulation of process it is necessary to select as the time unit the minimum characteristic time, for which there is a change in system. In this case it would be the characteristic hydrodynamic time.

Basically, any cellular automaton boils down to following points:

1. Finite number of states for cells.
2. Definition of a neighbourhood for each cell.
3. Rules of transition between the cell states.

The system considered here is an undirected graph, where each pore is corresponded to some vertex with the number i , and the edge $i - j$ means that there is an intersection between i -th and j -th pores. Let us denote by D_i the neighbourhood of i -th pore. State of each cell (pore) is defined by the energy barrier of outflow, which depends on the values of V , S_{neut} , S_{lg} and S_{ls} :

$$\delta A = \delta A(V, S_{neut}, S_{lg}, S_{ls})$$

Outflow from the pore i leads to change of the states of neighbouring pores, in other words $\delta A_k \xrightarrow{P} \delta A'_k$ for all pores in local configuration D_i . Here, P means the transformation of parameters V , S_{neut} , S_{lg} , S_{ls} in accordance with the change of the local configuration after emptying of i -th pore.

In this paper, two approaches in determining avalanches were used: the first one was called “Bak’s approach”, the second was corresponded to energy of avalanche. Let us explain what is meant by the first. Suggest that at some time t_k the outflow from the i -th pore occurs, and this pore has avalanche label n . This leads to change of local configuration of the i -th pore. Let for some pore j in this local configuration the energy barrier was $\delta A_j > 0$ before, and $\delta A'_j < 0$ after the outflow from the i -th pore. Then for this pore j label of avalanche n is assigned, and the power of the avalanche n is increased by 1. Otherwise, if the i -th pore initially has no avalanche label, then for i label of avalanche $M + 1$ is assigned, where M is the total number of avalanches at the moment. The energy of the avalanche is considered as the sum of energy changes for the local configurations in the avalanche:

$$E = \sum_{i=1}^s \left\{ \sum_{k=1}^{z_i} \delta E_k \right\}_i, \quad (6)$$

here, s – power of avalanche according to “Bak’s approach”, z_i – the number of filled neighbours of i -th emptied pore, δE_k – change of the surface energy of the k -th neighbour.

It is expected that both spectra should have power dependence, that is $N(s) \sim s^{-\beta}$ and $N(E) \sim E^{-\beta_{en}}$.

As it was mentioned above, in [3, 4] was made a guess about the self-organized criticality scenario of relaxation in “nonwetting liquid – nanoporous media” systems, which means the presence of some feedback mechanism. In this paper, the feedback mechanism is local: the outflow of liquid from pore leads to decrease of the barriers of pores in local configuration due to increase of “liquid – gas” surface, and avalanche-like evolution becomes possible, when outflow from one pore leads to outflow of liquid in some area. Analysis of avalanche size distribution could be an argument in favour or against of presence of self-organized criticality in such systems.

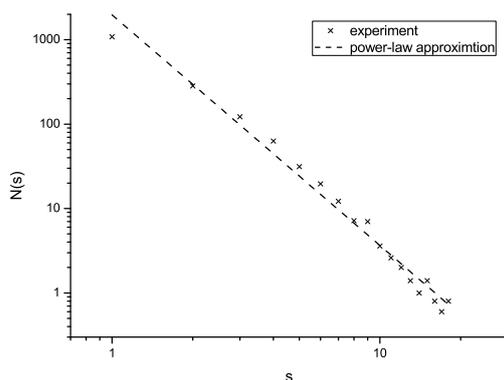


Figure 2. “Bak’s approach” avalanche size distribution in log-log scale.

Accordingly, avalanche size distributions were obtained for the system with Gaussian radii distribution (1, 0.28), average radius of pores $\bar{R} = 3$ nm, porosity $\varphi = 0.5$, $T = 293$ K, $\sigma = 72 \frac{\text{mJ}}{\text{m}^2}$, $\delta\sigma = 23 \frac{\text{mJ}}{\text{m}^2}$. In Fig. 2 avalanche size distribution, according to “Bak’s approach”, is shown. As it was expected, avalanches have a power-law distribution $N(s) \sim s^{-\beta}$, and $\beta = 2.73 \pm 0.08$. Coefficient of determination $R^2 = 0.9844$. It may be noted that the power of

avalanches does not reach an arbitrarily large value, and that there is some “downturn” in the end. This can be explained by the following factors:

1. Limited size of the system. Spreading, avalanche can reach the boundary of the system, after which the avalanche “movement” in this direction becomes impossible. This is especially important for pores near the border.

2. In this process the situation, when at one time several avalanches occur in different part of the system, is quite common. At the same time in calculating the power of avalanches it is assumed that they cannot merge or intersect. Thus, in reality not all of the volume available for the development of avalanches (or to be more precise, not all of the pores in this volume), but only the part limited by the “fronts” of other avalanches spreading at that moment.

3. Relatively small observation time and number of experiments. The probability of the occurrence of the avalanche of great power is really small, so to observe the avalanche with sizes of the order of system size the data sample must be much bigger.

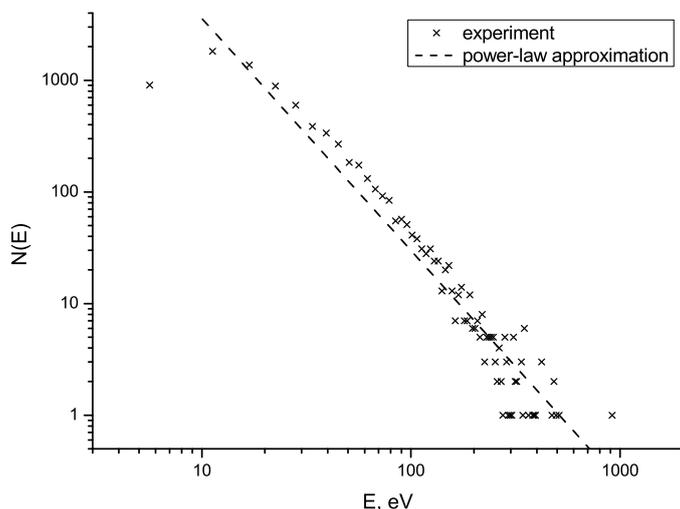


Figure 3. Distribution of avalanches’ energies in log-log scale.

Similarly, the energy spectrum of avalanches was obtained for the same parameters of the system. By assumption, it should also have power-law form. In Fig. 3 distribution of avalanches’ energies is shown in log-log scale. After excluding the first point, approximation gives a power dependence $N(E) \sim E^{-\beta_{en}}$ with $\beta_{en} = 2.25 \pm 0.16$ and coefficient of determination $R^2 = 0.9395$. Thus, typical for SOC phenomena power-law function provides a good approximation for both spectra.

3. Conclusion

Proposed cellular automaton allows to simulate relaxation process of “nonwetting liquid – nanoporous media” system with variety values of parameters σ , $\delta\sigma$, T , \bar{R} , ΔR , φ . In this paper, based on the described above local feedback mechanism, possibility of self-organized criticality in such systems was studied. For this purpose avalanche size and energy distributions were obtained. These spectra have a power-law form, which can be the evidence that proposed local feedback mechanism may indeed lead to self-organized criticality in this type of systems.

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