Eur. Phys. J. B **15**, 327–330 (2000)

THE EUROPEAN PHYSICAL JOURNAL B

EDP Sciences

Aging kinetics of porous media due to freezing-thawing cycles

K. Ivanova[a,b]

Institute of Electronics, Bulgarian Academy of Sciences, 72 Tzarigradsko chaussée, Sofia 1784, Bulgaria

Received 24 September 1999 and Received in final form 5 January 2000

Abstract. The two-dimensional Ausloos *et al.* model of fluid invasion, freezing and thawing in a porous medium is elaborated upon and investigated in order to take into account the pore volume redistribution and conservation during freezing. The results are qualitatively different from previous work, since the damaged pore sizes are found to be much less than the possible maximum value and is reached after a large number of invasion-freezing-thawing cycles, *e.g.* the material is "slowly damaged". The pore size distribution is thus found in better agreement with expected practical findings. The successive invasion percolation clusters are still found to be self-avoiding with aging. The cluster size decreases with a power law as a function of invasion-frost-thaw iterations. The aging kinetics is also discussed through the normalized totally invaded pore volume.

PACS. 05.40.-a Fluctuation phenomena, random processes, noise, and Brownian motion – 81.05.Rm Porous materials; granular materials – 81.40.Np Fatigue, corrosion fatigue, embrittlement, cracking, fracture and failure

1 Introduction

Water freezing in a porous material induces usually irreversible damage like fractures [1]. The internal pore structure is strongly affected by the stress field resulting from dilatation of the fluid under freezing [2]. The pore shape, sizes, volume distribution, connectivity, a.s.o. are many relevant technological parameters. Experimental and theoretical results are much lacking. The need for a more modern statistical physics framework and thinking approach is obvious [3,4]. While this phenomenon has been well studied through *e.g.* the so-called invasion percolation [5] and epidemic [6–8] models, the destructive effect of fluid freezing in the material has been less studied except through the recent model of Ausloos *et al.* [9,10].

Ausloos *et al.* considered a fluid invasion-frost-thaw cycle in a model porous material, basically assuming that the water volume [11] increases under freezing and modifies the elementary pore sizes. The distribution of pore sizes was seen to evolve with cycles toward the state in which all pores have the maximum size. The rule which governs the damage was such that the material was seen to be "rapidly damaged". A more moderate destruction process is suggested here by considering some volume constraint. A simple rule is thus defined in Section 2, taking into account the volume of each nearest neighboring pore. The volume of the freezing pore and its nearest neghbors is redistributed between them during freezing. Numerical investigations are reported in Section 3. The geometry of aged invasion clusters is illustrated as a function of time. Numerical results are presented and discussed, with respect to the pore size and number of filled pores distribution as a function of cycling time. I stress that the volume of the pore rather than their number is here the main concern. The kinetics of the invasion is also investigated. A discussion of open questions and some conclusion are drawn in Section 4.

2 Model

The model of reference [9,10] is used in order to serve as a basis for further developments under the more realistic constraint hereby introduced. A two-dimensional $L \times L$ square lattice represents the porous material and periodic boundary conditions are imposed. Each cell of the square lattice represents a pore. Each pore is connected with its four nearest neighbors. The starting size distribution is assumed to be flat and extending between zero and one. A random number $s_{i,j}$ is assigned to each pore with position (i, j). This number $s_{i,j}$ represents some measure of the pore size. The bottom of the lattice is then invaded by the fluid. Assuming that capilarity forces control the fluid invasion, the smallest pore in contact with the bottom layer is invaded first and the invasion follows such that at each time step, all empty pores in contact with the invaded pores are searched for and the pore having the minimum size is selected for invasion. The above selection-invasion rule is repeated until the fluid cluster reaches the top of the lattice.

[a] e-mail: kristy@ie.bas.bg

[b] *Temporary address*: Department of Meteorology, Pennsylvania State University, University Park, PA 16802, USA e-mail: kristy@essc.psu.edu

After invasion up to percolation, the fluid is assumed to freeze. The freezing pores are selected among the invaded pores going from left to right and from bottom to top layer. In order to simulate some damage due to freezing, the size of each invaded pore is assumed to increase according to the rule:

$$s_{i,j}^{+} = s_{i,j} + \varepsilon \frac{s_{i,j}}{\sum s_{i,j}} \tag{1}$$

where $\sum s_{i,j} = s_{i-1,j} + s_{i+1,j} + s_{i,j-1} + s_{i,j+1}$ is taken over the four nearest neighbors of the freezing pore $s_{i,j}$ and ε is a random number taken from a uniform distribution between zero and one. The size of each of the four neighbors decreases according to the rule (written for site $s_{i-1,j}$ as an example):

$$s_{i-1,j}^{+} = s_{i-1,j} \left(1 - \varepsilon \frac{s_{i,j}}{\left(\sum s_{i,j}\right)^2} \right). \tag{2}$$

According to equation (1) $s_{i,j}^{+}$ will always be greater than $s_{i,j}$. The maximum pore size of the frozen pores is also constrained to be always less than one, *i.e.* $s_{i,j}^{+} \in [s_{i,j}, 1]$. This requirement leads to the following restriction for ε:

$$\sum s_{i,j} \geq \varepsilon \frac{s_{i,j}}{1 - s_{i,j}} \cdot \tag{3}$$

In doing so the total pore volume is conserved. The invasion-freezing-thawing process is repeated a large number n of times. The parameter n can be associated with a time scale. Iterations up to $n = 100$ have been simulated. I have investigated $L \times L$ lattices with L varying from 100 to 500. The following data results from a compendium of several cases. The semi-quantitative aspects have been found to be stable with respect to changes in numerical parameters.

Clusters of damaged porous material after invasion and thawing for various time steps are studied. It is clear that the successive invasion percolating clusters seem to follow the rule found in references [9,10], *i.e.* they are quasi self-avoiding, and thinning as n increases. A set of examples is shown in Figure 1 at large time steps of evolution.

3 Evolution of the porous material

The number of invaded/filled pores $N_{\text{fill}}(n)$ as a function of time step n is shown in Figure 2 for n up to 100. It results from an averaging over 15 simulations. Starting from a flat size distribution between zero and one, the distribution $N_{\text{fill}}(s)$ changes as n increases (Fig. 3). In contrast to the papers of Ausloos *et al.*, in which the shape of the distribution $N_{\text{fill}}(s)$ piles up into a maximum for the maximum size $s = 1$ after 12 iteration cycles, the distribution is here evolving toward a maximum size much lower than unity. Also the distribution increases for small sizes and presents a wide dip between 0.2 and 0.4. This behavior looks like that found in real situations where (i) classes of small pores do not disappear since many small pores are supposedly appearing when a large one breaks, and (ii) classes of large pores are unaffected (since they are not invaded) for large n values. Notice that the shape of the curve seems not to change qualitatively between $n = 20$ and $n = 100$.

It is interesting to see how the size distribution evolves after a few damages. The size distribution $V_{\text{ini}}(s)$ of available pore volume before the n th invasion is shown in Figure 4. Notice that most of the available volume piles up at the size where $N_{\text{fill}}(s)$ is maximum. There is a slight evolution with the pore size as some stable region appears for $n = 20$ till 100.

It is of capital interest to understand the cluster size aging. In order to do so the sum of filled volumes normalized to the total initial volume after a given cycle has been measured as a function of time n and as a function of the size s distribution. The former is shown in Figure 5. It appears that the sum of filled pores is first linearly decreasing, but then saturates at large n. Moreover from Figure 6, it appears that the integrated invaded/filled volume is decreasing with the number of iteration steps. Larger and larger pores can be invaded with increasing n.

4 Discussion and conclusion

The percolation cluster evolution of the percolation cluster size S as a function of n is found to decrease as a power law

$$S \sim n^{-\delta}. \tag{4}$$

For 200×200 lattices the exponent $\delta = 0.25 \pm 0.04$ (the inset of Fig. 2) in contrast to the case of reference [10] where it is 0.4. The value depends on the lattice size L increasing logarithmically with L. It has not been searched for whether the model leads to a fractal or a multifractal case. The evolution of the fractal dimension of percolating clusters is usually very slow and is quite close to a logarithmic decrease. Such a slow power law is a characteristic of aging and high order correlation in phase transitions.

In summary, I have extended a very simple model of porous material degradation *via* fluid invasion, frost and thaw cycles toward a more realistic case than previously, *i.e.* there is some fluid volume conservation during freezing. The fluid transport is based on the invasion percolation model.

The porous material is found to be less rapidly damaged than in Ausloos *et al.* papers. The form of the pore age distribution is also quite different. However, the investigations of the cluster geometry have shown that there is still a slow evolution after several invasion-freeze-thaw cycles in agreement with experimental works.

I gratefully thank M. Ausloos for pointing out different aspects of this study and for instructive discussions. Dr. A. Erzan is thanked for critical reading as well.

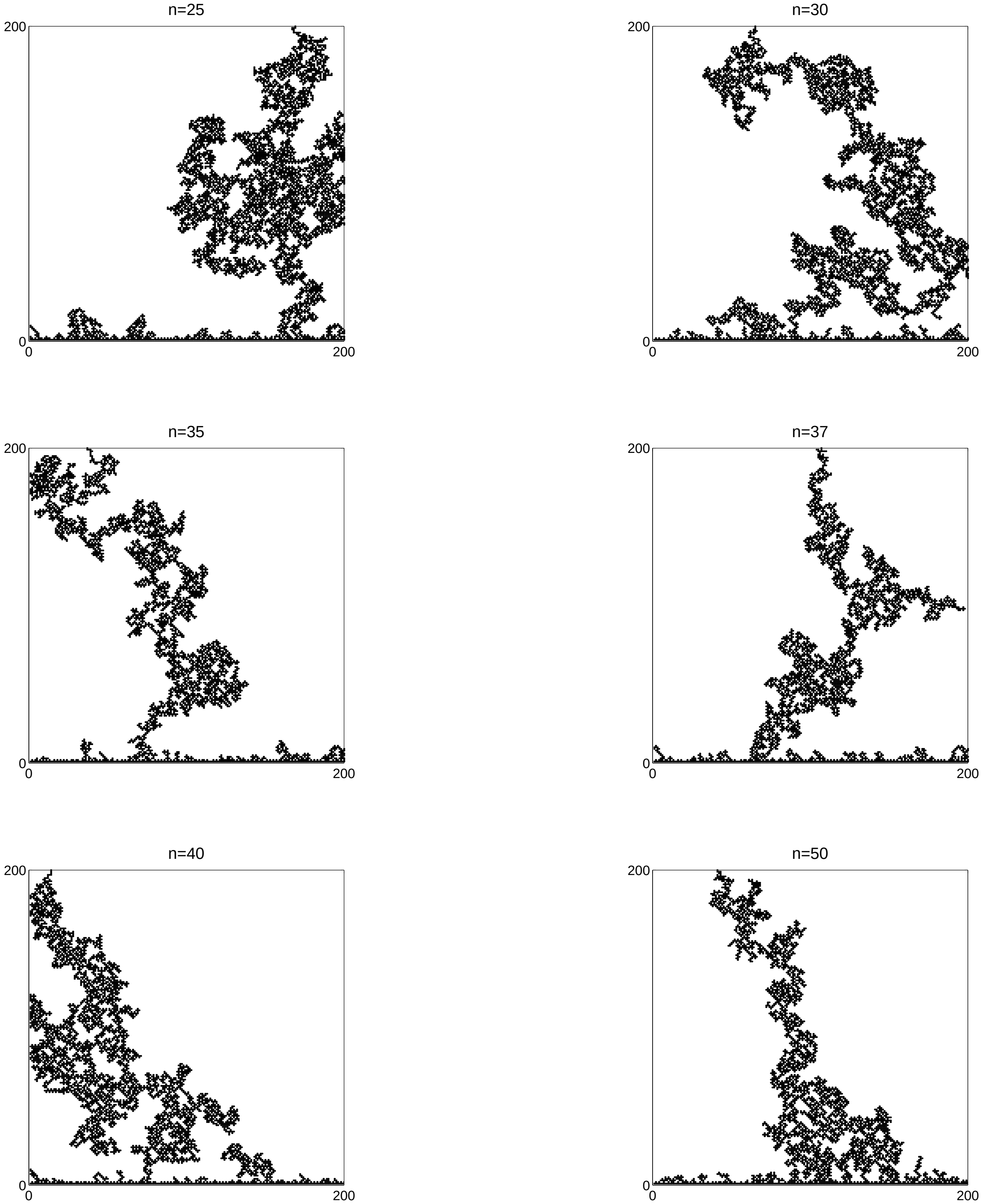

Fig. 1. Snapshots of the evolution of the percolation cluster as a function of the invasion-frost iteration time n at various n.

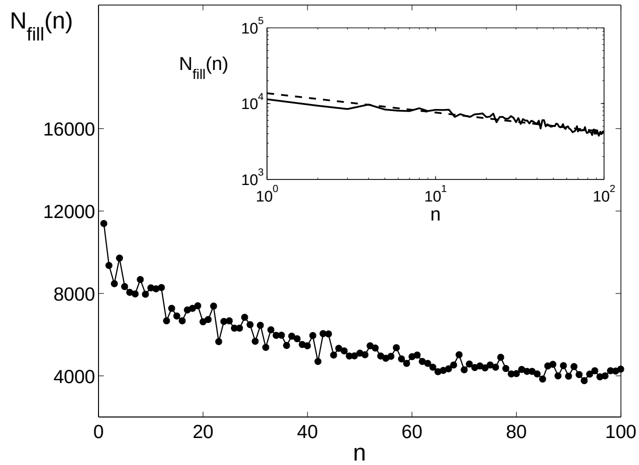

Fig. 2. The number distribution $N_{\text{fill}}(n)$ of filled pores for different iterations n up to 100. Inset: Log-log plot of the number distribution $N_{\text{fill}}(n)$ of invaded pores as a function of n, less than 100, thereby giving the exponent $\delta = 0.25$.

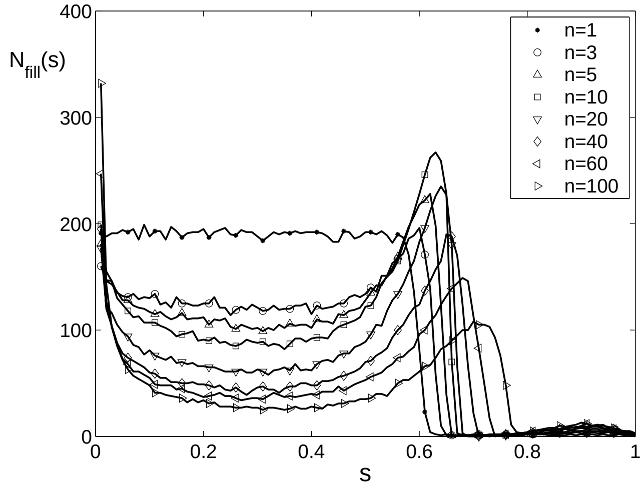

Fig. 3. The size distribution of $N_{\text{fill}}(s)$ filled pores after different iterations n.

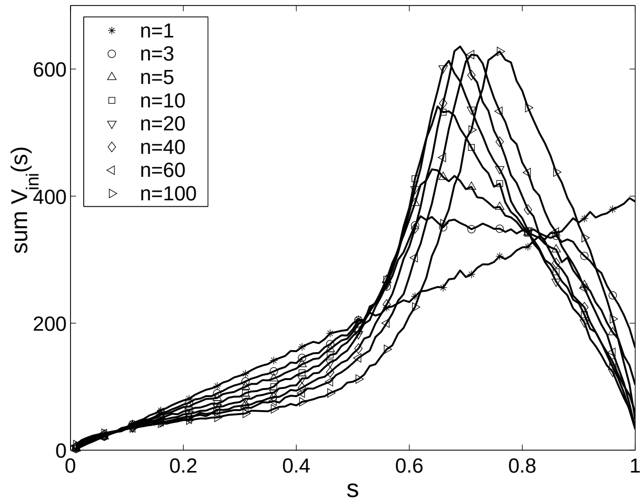

Fig. 4. Normalized distribution of the sum of initially available pore volumes sum$V_{\text{ini}}(s)$ in the material as a function of size s at different n times.

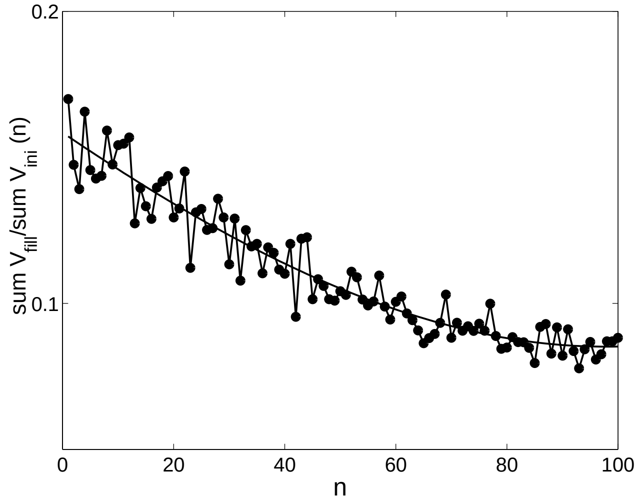

Fig. 5. Distribution of normalized total volume of filled pores.

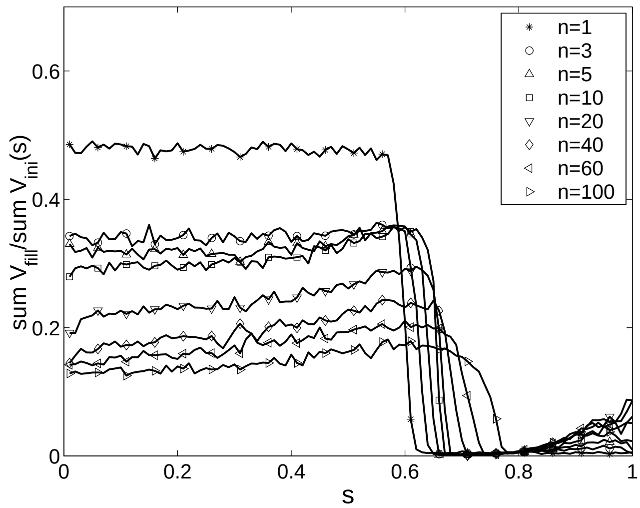

Fig. 6. Distribution of normalized sum of filled volumes as a function of pore size.

References

1. M. Nakamura, T. Fukushima, M. Kamitani, J. Ceram. Soc. Jpn **100**, 853 (1992).
2. J.R. Blachere, J.E. Young, J. Amer. Ceram. Soc. **55**, 306 (1972).
3. D. Stauffer, A. Aharony, *Introduction to Percolation Theory*, 2nd edn. (Taylor & Francis, London, 1994).
4. M. Sahimi, *Flow and Transport in Porous Media and Fractured Rock* (VCH, Weinheim, 1995).
5. L. Furuberg, J. Feder, A. Aharony, T. Jøssang, Phys. Rev. Lett. **61**, 2117 (1988).
6. A. Bunde, H.J. Herrmann, A. Margolina, H.E. Stanley, Phys. Rev. Lett. **55**, 653 (1985).
7. N. Vandewalle, M. Ausloos, Phys. Rev. Lett. **77**, 510 (1996).
8. K. Ivanova, Phys. Rev. E **57**, 4827 (1998).
9. M. Ausloos, E. Salmon, N. Vandewalle, Cement Concrete Research **29**, 209 (1999).
10. E. Salmon, M. Ausloos, N. Vandewalle, Phys. Rev. E **55**, R6348 (1997).
11. M. Ausloos, Phys. Rev. E (to be published, 2000).