PHYSICAL REVIEW E VOLUME 55, NUMBER 6 JUNE 1997

Aging of porous media following fluid invasion, freezing, and thawing

E. Salmon, M. Ausloos,* and N. Vandewalle
SUPRAS, Institut de Physique B5, Université de Liège, B-4000 Liège, Belgium

(Received 24 February 1997)

A simple model of fluid invasion, freezing, and thawing in a porous medium is elaborated and investigated. This model is based on the invasion percolation model. The fluid freezing process is considered to destroy the internal structure of the porous medium. The evolution of the pore structure after several invasion-frost-thaw events (cycles) has been investigated numerically. The results are qualitatively consistent with experimental findings. The cluster size decreases with a power law as a function of invasion-frost-thaw iterations. Moreover, the geometry (fractal dimension) of percolating invasion clusters varies with the number of cycles. The successive percolation clusters are found to be self-avoiding with aging. [S1063-651X(97)50506-X]

PACS number(s): 61.43.Gt, 05.40.+j, 81.05.Rm, 81.40.Np

I. INTRODUCTION

The invasion of a fluid in porous media is a subject of high interest in the statistical physics community, since notions like percolation and growth phenomena are involved [1,2]. While this phenomenon has been well studied through, e.g., the so-called invasion percolation [3] and epidemic [4,5] models, the destructive effect of fluid freezing in the material has been less studied.

Several studies [6] have shown that the freezing of water in a porous material induces usually irreversible damage like fractures. Indeed, the internal pore structure is strongly affected by the dilatation of the invading fluid under freezing. At the microscopic pore level, the freezing mechanism is a very complex phenomenon involving numerous parameters like the pore shape, the pore connectivity, the pore distribution, etc. [7] A well established statement is that the smaller a pore is, the more damaged it will usually become after freezing [8]. However, these studies are actually restricted to a few experimental and rather empirical results. There is a lack of theoretical or numerical studies about the material frost resistance, and the need for a more modern statistical physics framework and thinking.

The aim of the present paper is to introduce and study a simple model of the fluid invasion-freezing-thawing cycle in a porous material. From this, we study the aging of the porous material after several invasion-freeze-thaw cycles under simple rules. The most simple one is illustrated below, and described in Sec. II. It consists basically of assuming that the water density increases under freezing, and modifies (extends) the pore size. Other cases (see Sec. II) have been examined without giving any other spectacular difference with respect to those given below. Thereafter, the numerical results are presented and discussed. The kinetics of the invasion are investigated in Sec. III. The geometry of aged invasion clusters are investigated in Sec. IV. Conclusions are drawn in Sec. V.

*Corresponding author.
Electronic address: ausloos@gw.unipc.ulg.ac.be

II. MODEL

The model is assumed to be as simple as possible in order to serve as a basis for further developments under more realistic constraints. The model is inspired from the well-known invasion percolation model [3] and subsequent ideas from kinetic growth models [9]. An $L\times L$ square lattice with vertical periodic boundary conditions represents the porous material. Each cell of the square lattice represents a pore. Each pore is connected with its four nearest neighbors. A random number r_i between 0 and 1 is assigned to each pore i. This number r_i represents some measure of the pore size. In the present model each pore is characterized only by that number whatever its real size, surface, shape, etc. We are obviously aware that a mere set of numbers on a square lattice is a drastic approximation for modeling a real porous structure [2]. See Ref. [10] for a list of other network models.

The initial configuration of a 5×5 lattice is represented in Fig. 1(a). The bottom of the lattice is then invaded by the fluid. Assuming that capilarity forces control the fluid invasion, the small pores are invaded first. The invasion rule is thus the following. At each time step, all empty pores in contact with invaded pores are selected. In this set of selected pores, the pore having the minimum size is assumed to be invaded. The above selection-invasion rule is repeated until the fluid cluster reaches the top of the lattice. The first percolation cluster resulting from the 5×5 lattice of Fig. 1(a) is drawn in Fig. 1(b). The labels in the bottom corner of each

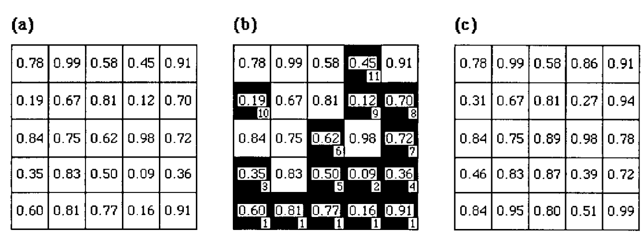

FIG. 1. Illustration of the invasion-freezing process: (a) A 5×5 lattice representing the porous material. (b) The invasion of the porous material by a fluid (represented in dark); the labels give the evolution of this invasion. (c) The porous structure after the freezing process.

invaded cell indicate the different time step at which the invasion has taken place.

After invasion up to percolation, the fluid is assumed to freeze. In order to simulate some damage due to freezing, the size of each invaded pore is assumed to increase according to the following rule:

$$r_i \rightarrow r_i + \epsilon(1-r_i) \tag{1}$$

where ϵ is a random number taken from a flat distribution between zero and one. In so doing, $r_i(t+1)$ is always in $[r_i(t),1]$. In some sense, this presupposes that the pore size itself follows the variation of the water density under freezing. Other cases have been studied like a variation $dr/dt \sim t^{-\beta}$, but it does not bring anything drastically different on the aging overall physical behavior (see below); however, the pore size distribution may evolve according to different laws. Thus, for simplicity and conciseness, we keep the evolution of Eq. (1) as a paradigm.

An example of a damaged porous material after the invasion corresponding to that of Fig. 1(b) is drawn in Fig. 1(c). The frozen fluid is then assumed to thaw following Eq. (1), and the material to be completely dried up. A new fluid invasion can then take place.

The invasion-freezing-thawing process is repeated a large number n of times. For natural or artificial porous rocks, the parameter n can be associated with a time scale, like a number of years in extreme climatic conditions (cold winter for freezing and hot summer for complete water removal). In the laboratory, the cycles n are used to estimate the frost resistance of some material [8].

We have investigated $L\times L$ lattices with L varying from 10 to 500. Iterations up to $n=200$ have been simulated. This iteration n values are realistic numbers with respect to available experimental tests and reports [11]. The following data are a compendium of sometimes more than 100 cases.

III. EVOLUTION OF THE POROUS MATERIAL

From Eq. (1), one would expect that the size of a given pore i reaches exponentially unity, i.e.,

$$r_i = 1-\exp(-t/2), \tag{2}$$

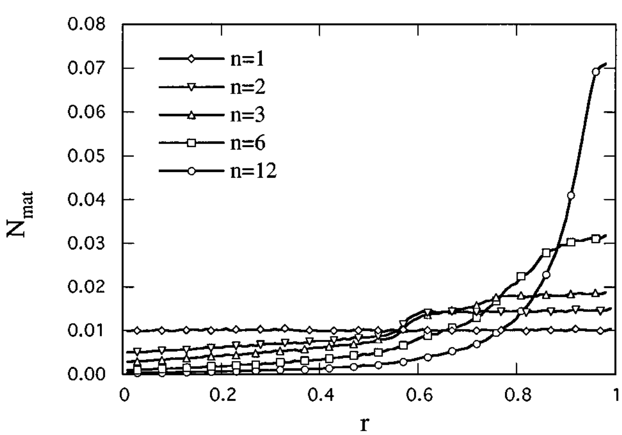

FIG. 2. The normalized distribution of pore sizes $N_{\mathrm{mat}}(r)$ in the material after different invasion damages: $n=1$, 2, 3, 6, and 12.

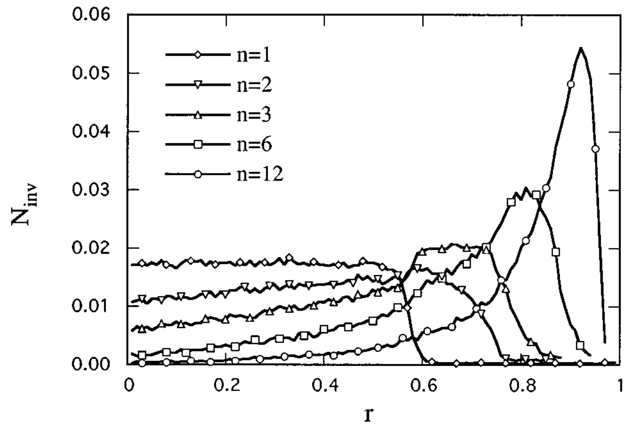

FIG. 3. The size distribution $N_{\mathrm{inv}}(r)$ of invaded pores after different iterations $n=1$, 2, 3, 6, and 12.

where t is the number of times that the pore is invaded and damaged. Thus the material is expected to be ''rapidly damaged.''

Figure 2 presents the normalized distribution of pore sizes $N_{\mathrm{mat}}(r)$ after different invasion-damage but before the freezing $n=1$, 2, 3, 6, and 12. From a distribution which is initially a flat distribution between 0 and 1, the distribution becomes narrow near unity as n increases. The shape of the distribution $N_{\mathrm{mat}}(r)$ is exponential for large n values, as expected from Eq. (2). This behavior looks like real situations where classes of small pores seems to disappear with n, while classes of large pores become more important for large n values of freezing-thawing cycles [6].

Another interesting set of findings pertains to the size distribution $N_{\mathrm{inv}}(r)$ of invaded pores for different iterations $n=1$, 2, 3, 6, and 12 as drawn in Fig. 3. For $n=1$, this distribution is flat between 0 and a threshold ($r_c^{(1)}\approx 0.55$). As n increases, the distribution of invaded pores $N_{\mathrm{inv}}(r)$ presents a smooth increase with a soft maximum above the $r_c^{(1)}$ threshold. As n further increases, the distribution becomes an exponential law similar to the $N_{\mathrm{inv}}(r)$ distribution, but still showing a threshold at $r_c^{(n)}$. This threshold $r_c^{(n)}$ evolves exponentially towards unity with n. In fact, one can verify that

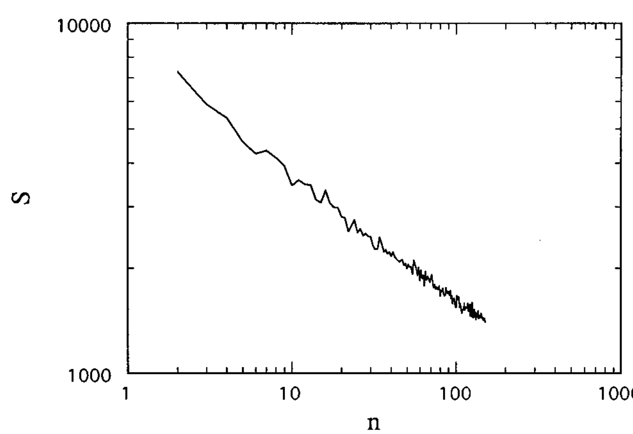

FIG. 4. Evolution of the cluster size as a function of the invasion-frost iterations n. Each dot is an average over 100 simulations. The lattice size is 200×200.

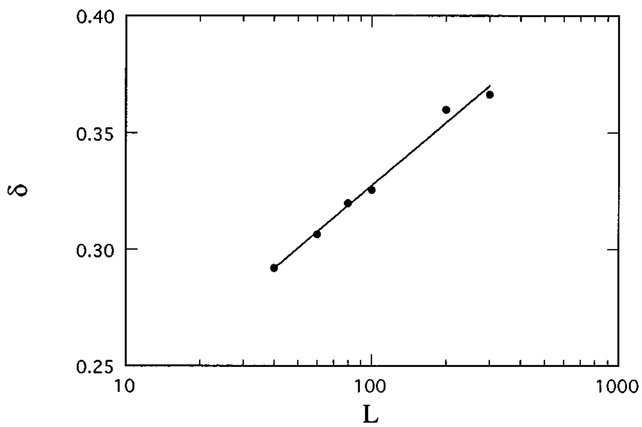

FIG. 5. The exponent δ of the percolation cluster size evolution $S(n)$ as a function of the lattice size L in a semilog plot. The continuous line represents a logarithmic fit $\delta \sim \ln(n)$.

the $N_{\mathrm{inv}}(r)/N_{\mathrm{mat}}(r)$ ratio is flat for any n between $r=0$ and the threshold $r_c^{(n)}$.

IV. INVASION CLUSTER GEOMETRY

Since the pore size distribution evolves as such in the material, the fluid has to invade larger and larger pores as n increases. In experimental situations, the quantity of water invading a porous material increases effectively with invasion-frost-thaw iterations [11].

It is of interest to investigate the cluster size aging. Figure 4 presents the evolution of the percolation cluster size S as a function of n for 200×200 lattices. In the investigated range of n, the cluster size S is found to decrease as a power law,

$$S \sim n^{-\delta}. \tag{3}$$

This extremely slow evolution was observed experimentally [11]. In these experiments, evolving structures have been still observed after more than 10 000 freezing-thawing cycles indeed. The exponent δ depends on the lattice size L (Fig. 5), and is seen to increase logarithmically with L for the range of n values investigated herein.

Figure 6 presents the percolating cluster for each of the first six iterations ($n=1$, 2, 3, 4, 5, and 6). For $n=1$, the cluster is of course equivalent to a classical invasion percolation cluster. For $n>1$, the cluster size decreases with n. Moreover, the cluster seems to grow in an anisotropic fashion with n, i.e., the cluster looks more and more stretched as n increases. This is well seen for the $n=3$ cluster in Fig. 6. However, loops and dead ends are still present in these anisotropic clusters at each iteration.

An additional relevant observation is that the successive invasion percolating clusters seem to be as if they were quasi-self-avoiding. This effect is well noticed in Fig. 6, where n and $n+1$ clusters have invaded different regions of the material.

For $n=1$, the percolation cluster is fractal [3], with a fractal dimension $D_f=91/48\approx 1.89$. Since the percolation cluster size decreases with n and the cluster becomes anisotropic, the fractal dimension of such clusters should decrease with n. In order to estimate D_f, we have measured the cluster size for different lattice sizes $L\times L$ and for different iterations n. Assuming the relationship

$$S \sim L^{D} f, \tag{4}$$

we have extracted the fractal dimension D_f of the percolating clusters as a function of n. Figure 7 presents in a log-log plot the evolution of D_f as a function of n. The fractal dimension of percolating clusters seems to decrease logarithmically from $D_f=\frac{91}{48}$ as

$$D_f = 1 + \tfrac{43}{48} n^{-\gamma}, \tag{5}$$

reaching $D_f=1$ for $n\to+\infty$. The continuous line in Fig. 7 is a fit giving $\gamma=0.067\pm0.006$. Since this exponent is small, the evolution of the fractal dimension of percolating clusters is very slow, and is quite close to a logarithmic decrease ($\gamma=0$). Such a slow power law is a characteristic of aging and high-order correlation in phase transitions [12]. From

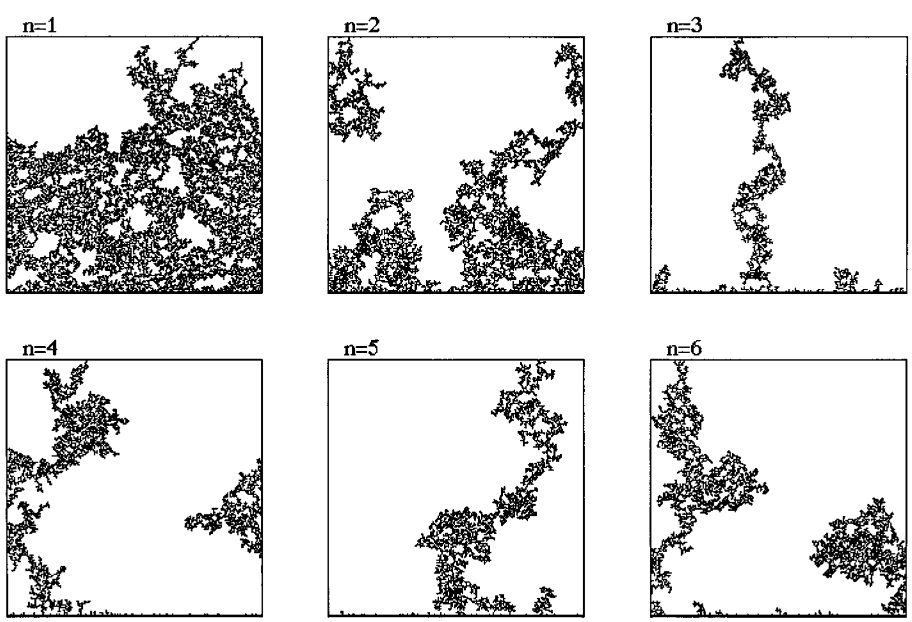

FIG. 6. Successive percolating clusters observed on a 200×200 lattice after $n=1$, 2, 3, 5, and 6 iterations.

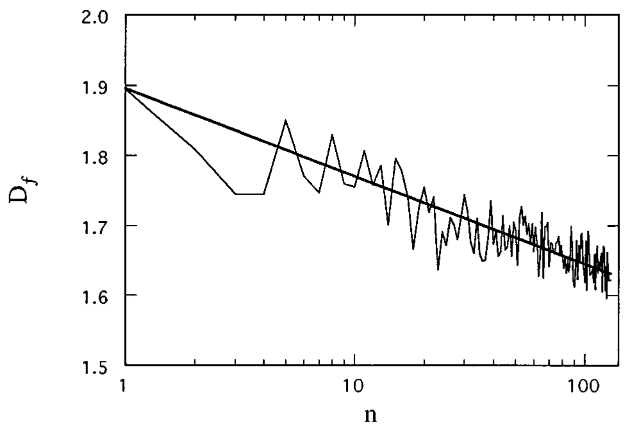

FIG. 7. The fractal dimension D_f of percolating clusters as a function of the number of cycles ($n<200$) in a log-log plot. The continuous line is a fit with Eq. (5).

Eqs. (3) and (5), one has $\delta \sim \ln(L)$ for values of n less than L. This weak logarithmic dependence is that represented by the continuous line drawn in Fig. 5.

V. CONCLUSION

We have introduced and investigated a very simple model of porous material degradation via several fluid invasion, freezing, and thawing cycles. The fluid transport is based on the invasion percolation model. The development of the model toward a more realistic one with other constraints is obviously feasible.

The porous material is found to be rapidly damaged with invasion-freeze-thaw cycles. We determined the form of the pore age distribution. The size $r_c^{(n)}$ of the largest pore invaded by the fluid reaches unity exponentially. However, 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. Other assumptions for the damage rule of the material can lead to other laws for the evolution of the pore size distribution. However, the geometrical properties of the clusters present the same slow evolution.

A very interesting point from a strict statistical point of view is that a memory or aging effect is discovered for the percolating clusters. Indeed, the successive cluster growth seems to take place in different regions of the material, i.e., successive clusters are self-avoiding. This effect is unchanged if one uses other damaging laws instead of Eq. (1). The self-avoiding cluster behavior has an interesting signature in the fractal dimension of the percolating cluster. This observation merits to be a subject of further investigations, e.g., in higher dimensions.

ACKNOWLEDGMENTS

This work was partially supported through CSTC-KUL-ULg contract (IRSIA CI/1/4-8828/218; CIB-218; RW 2843; IWT RD/94/06-F02), and the ARC (94-99/174) contract of the University of Liège. A special grant from FNRS/LOTTO allowed us to perform specific numerical work. Thanks to R. Gérard, F. de Barquin, J. Elsen, and N. Lens (CSTC) for instructive discussions, for their constant interest, and for informing us of data prior to publication [8].

[1] D. Stauffer and A. Aharony, *Introduction to Percolation Theory*, 2nd ed. (Taylor & Francis, London, 1994).
[2] M. Sahimi, *Flow and Transport in Porous Media and Fractured Rock* (VCH, Weinheim, 1995).
[3] L. Furuberg, J. Feder, A. Aharony, and T. Jøssang, Phys. Rev. Lett. **61**, 2117 (1988).
[4] A. Bunde, H. J. Herrmann, A. Margolina, and H. E. Stanley, Phys. Rev. Lett. **55**, 653 (1985).
[5] N. Vandewalle and M. Ausloos, Phys. Rev. Lett. **77**, 510 (1996).
[6] M. Nakamura, T. Fukushima, and M. Kamitani, J. Ceram. Soc. Jpn. **100**, 853 (1992).
[7] J. R. Blachere and J. E. Young, J. Am. Ceram. Soc. **55**, 306 (1972).
[8] N. Lens, R. Gérard, F. de Barquin, and J. Elsen, CSTC Mag. (Brussels) **3**, 12 (1996).
[9] H. J. Herrmann, Phys. Rep. **136**, 153 (1986).
[10] R. Hilfer, in *Advanced Chemistry Proceedings*, edited by I. Prigogine and S. A. Rice (Wiley, New York, 1996), Vol. XCII, pp. 350–353.
[11] H. Bentrup, Ph.D thesis, Technical University Hamburg-Harburg, 1992.
[12] H. E. Stanley, *Phase Transitions and Critical Phenomena* (Clarendon, Oxford, 1971).