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“Burning and sticking” model for a porous material: suppression of the topological phase transition due to the backbone reinforcement effect

A. S. Ioselevich, D. S. Lyubshin

Landau Institute for Theoretical Physics RAS, 117940 Moscow, Russia,

Moscow Institute of Physics and Technology, 141700 Moscow, Russia

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We introduce and study the “burning-and-sticking” (BS) lattice model for the porous material that involves sticking of emerging finite clusters to the mainland. In contrast with other single-cluster models, it does not demonstrate any phase transition: the backbone exists at arbitrarily low concentrations. The same is true for hybrid models, where the sticking events occur with probability q: the backbone survives at arbitrarily low q. Disappearance of the phase transition is attributed to the backbone reinforcement effect, generic for models with sticking. A relation between BS and the cluster-cluster aggregation is briefly discussed.

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Single-cluster models of random porous networks which take into account physical requirements of mechanical stability on all stages of the system preparation process are promising candidates for adequate description of realistic porous materials, such as porous metals [1], gels [2], aerogels [3], etc. The simplest single-cluster models were introduced and studied in [4, 5]. In these models finite clusters arising in the process of gradual destruction of randomly chosen bonds and/or sites in the system are immediately “repaired” by means of regeneration of the critical bond/site whose destruction has lead to violation of connectivity. The model with randomly removed (and sometimes regenerated) bonds is the self-repairing bond percolation (SRBP) model; the model with randomly removed sites is the self-repairing site percolation (SRSP) model. In both models the system consists of a single infinite cluster at all accessible concentrations. However, the topological properties of this cluster undergo dramatic changes at a certain critical concentration: the *backbone* of the infinite cluster disappears and the system occurs in a peculiar tree-like state with anomalous mechanical and electrical properties caused by the fractal character of this state. We remind here that the backbone is defined as an infinite doubly connected component of an infinite cluster, or, equivalently, as an infinite *block* on the corresponding graph (for the definition of the term *block*, see, e.g. [6]). Physically, the backbone is a current-bearing substructure of the infinite cluster (see, e.g., [7, 8]). Note that the existence of an infinite cluster without a backbone is a very unusual phenomenon, which is not observed in standard percolation models.

This finite concentration phase transition is also present in a one parameter family of hybrid models (which we call SR(S/B)P). In this case at each step of the sample manufacturing process, with probability $1-Q$ a randomly chosen bond is removed (and then restored if necessary) and, with probability Q, a randomly chosen site together with all adjacent bonds is removed (and then restored if necessary). The properties of the phase transition are, however, non-universal within the SR(S/B)P family: for example, the fractal dimension D_B of the backbone near the threshold depends on the parameter Q (see [5]).

The site/bond regeneration can only roughly reproduce a realistic process of manufacturing a porous material. Schematically this process is as follows: a homogeneous mixture of matrix material grains and grains of a pore-former (carbon, which can be burned out, or a soluble polymer) is prepared; then the pore-former grains are gradually removed. Finite clusters arising in the process of the pore-former removal immediately fall off and stick to the surrounding matrix (see Fig.1). It means, in particular, that the restored bond is not necessarily identical to the removed one. Moreover, the number of newly created bonds is larger than one: to establish mechanical stability the cluster should stick to the matrix at exactly D (D being the space dimension) points. Would the phase transition be also present for such realistic process?

To answer this question in this paper we introduce another lattice single-cluster model: the “burning-and-sticking” (BS) one. As in the SRSP model, grains initially occupying all sites of certain regular lattice are

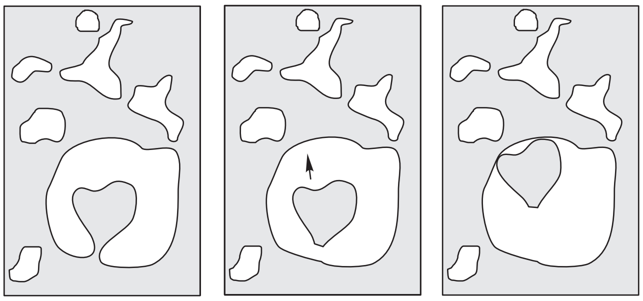

Fig.1. "Realistic" pore forming process. Left panel: just before a cluster detachment; there is only a thin bridge connecting the peninsula with the mainland. Middle panel: The bridge is burned, the island detaches from the mainland and moves toward the wall of the cavern in the direction of the arrow. Right panel: The island safely sticks to the wall at two points

removed ("burned") at random, and finite clusters occasionally created in the burning process are immediately repaired. However, the repairing procedure which is launched after detachment of each finite cluster is different from the SRSP one. Namely, the disconnected cluster is shifted in a randomly chosen direction until it sticks to the mainland (Fig.2). In the case of a lattice

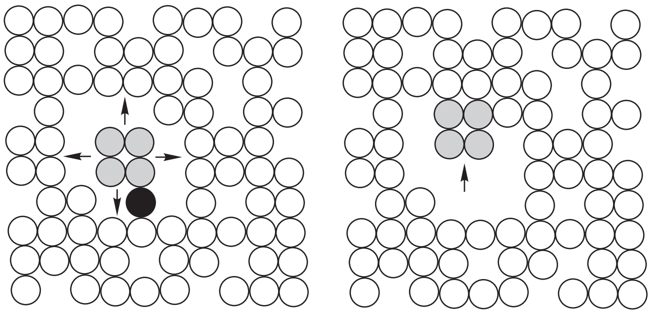

Fig.2. The repairing procedure for the "burning-and-sticking" model (BS) on a square lattice. The black grain is appointed for burning at a certain step, and a finite cluster (shown grey) is ready to be detached (left panel). This cluster is then shifted in one of four crystallographic directions shown by arrows, and sticks to the rest of the system (right panel)

model (which is only discussed in this paper) the direction of the shift is chosen from a discrete set of crystallographic axes, so that upon sticking all grains occupy sites of the same lattice, and the process can go on.

In Fig.3 we show the concentration dependence of the backbone density $P_B(x)$ as obtained from simulations of the BS model on the square lattice using $L \times L$ samples. The backbone clearly exists for all $x > 0$, and at small x its density vanishes as

$$P_B(x) \propto x^{\beta_B}, \tag{1}$$

with $\beta_B^{(\mathrm{BS})} \approx 2.85(15)$.

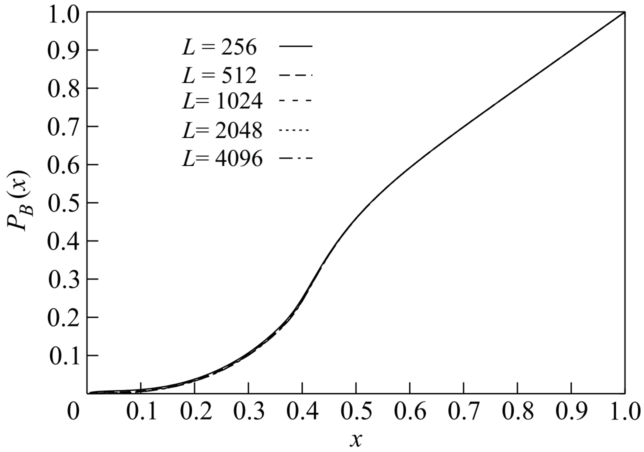

Fig.3. Backbone density vs concentration of sites for BS model with samples of different sizes L. The curves almost merge for $L > 512$. There is clearly no phase transition at any finite x

A fragment of the BS-pattern at relatively low concentration $x = 0.2$ is shown in Fig.4. One notices that

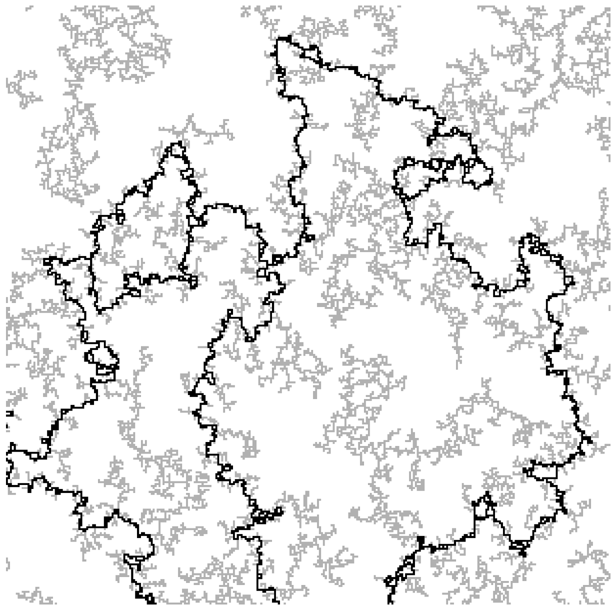

Fig.4. Snapshot of a BS-system at site concentration $x = 0.2$. Backbone has density 0.02742 and is shown black, dangling ends are shown grey. Fragment of size 309×306

the density of the entire cluster looks much more homogeneous than that of the backbone. Hence, one can expect that the correlation radius for total density $\xi_D(x)$ diverges slower than that for the backbone $\xi_B(x)$. The presence of two different scales $\xi_D(x) \ll \xi_B(x)$ presumably should make the low-density behavior of the BS model very rich. This issue is under study now.

The morphology of three infinite clusters – for standard percolation, SRSP, and BS models at the same density $P = 0.15$ – is compared in Fig.5 (left column).

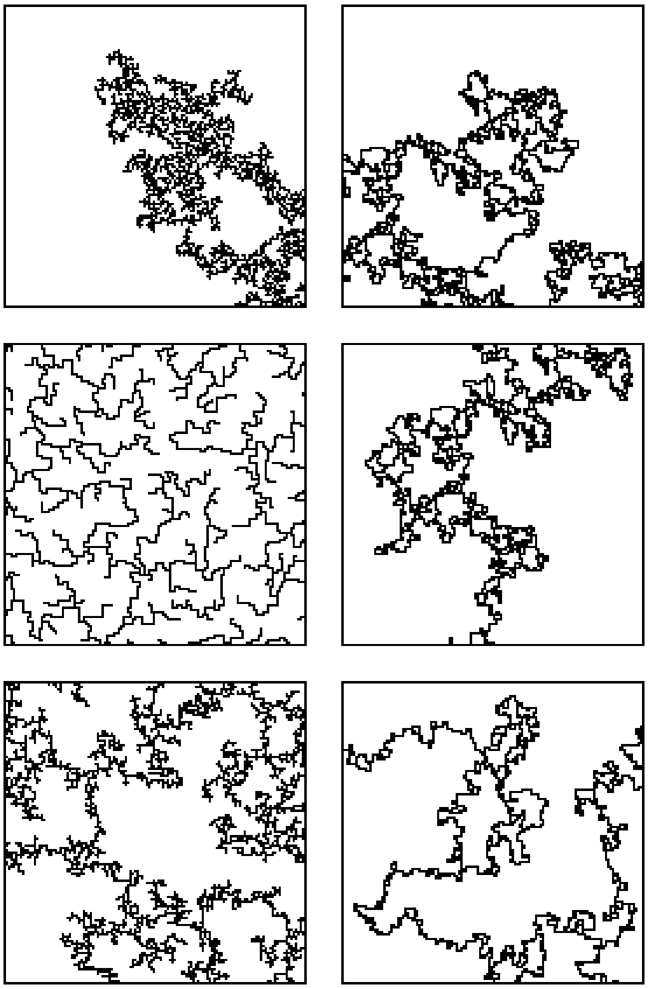

Fig.5. Comparative morphology of standard site percolation (upper line), SRSP model (middle line), and BS model (lower line). Left column: fragments of infinite clusters at the same density $P = 0.15$. Right column: fragments of backbones at the same density $P_B = 0.1$. All fragments of size 128×128

The difference between standard percolation and SRSP is striking: for percolation the infinite cluster is strongly inhomogeneous, with loops and dangling ends of all sizes, while for SRSP it is much more homogeneous, practically loop-less, and apparently single-wired on scales $r < \xi_0$, where ξ_0 is some nontrivial "branching length". We expect $1 \ll \xi_0 \ll \xi_D$ at $x \ll 1$. Properties of the infinite cluster for BS model are somewhere in between, though closer to SRSP.

A similar comparison of three backbones at the same density $P_B = 0.1$ is made in Fig.5 (right column). There is no qualitative difference between percolation and SRSP backbones, while the BS backbone is very special: it seems to have a "short-haired" and almost single-wired structure: there are large loops (of sizes $\sim \xi_B$) constituting a single-wired frame of the backbone. The wires of this frame are dotted with very small loops (of sizes ~ 1), while there are almost no loops of intermediate sizes. This is especially well seen on backbones of very low density ($P_B \sim 10^{-3}$, not shown).

Thus, the properties of the BS model are very different from those of SRBP, SRSP and their hybrids: the finite density topological phase transition, always present for all models of the SR(S/B)P family, does not show up in BS. The reason for this effect is apparently "backbone reinforcement" that accompanies sticking events in the lattice BS models. Indeed, a finite cluster is produced when the last bridge connecting it to the mainland is destroyed. Upon sticking, however, not necessarily one but possibly many new bridges are created: the larger is the cluster, the more. These new links establish new paths that cross the cluster and connect two opposite shores of the mainland. As a result, connectivity of the infinite cluster increases and its backbone strengthens.

The backbone reinforcement effect on the lattice seems to be dramatically enhanced compared to the case of a real continual physical system due to a special geometric resonance. A huge number of new bonds regenerated in a single sticking event is obviously an artifact of a lattice: it is only possible on a lattice that many grains belonging to the cluster simultaneously come in touch with the grains of the mainland. For a continual system mechanically stable contact of the cluster with the mainland would typically be established at exactly D points.

A question arises if the observed suppression of the phase transition in the BS model is a consequence of this artificially strengthened backbone reinforcement. Can the transition show up again in models with more realistic moderate reinforcement effect?

To address this question we started from a study of a family of hybrid BS-SRSP models in which the repairing of the finite cluster is performed according to the SRSP scenario with probability $1 - q$ and according to the BS scenario with probability q. The corresponding backbone densities are shown in Figs.6, 7. Although for $x > x_c^{(\mathrm{SRSP})}$ curves do not differ much from the SRSP curve, for $x < x_c^{(\mathrm{SRSP})}$ nonzero backbone density is found for all $q > 0$. The low density behavior of P_B is still governed by the power law (1), but with q-dependent index $\beta_B(q)$, shown in Table. Probably $\beta_B(q)$ diverges as $q \to 0$.

Thus, already an infinitesimal involvement of the BS process destroys the phase transition and revives the

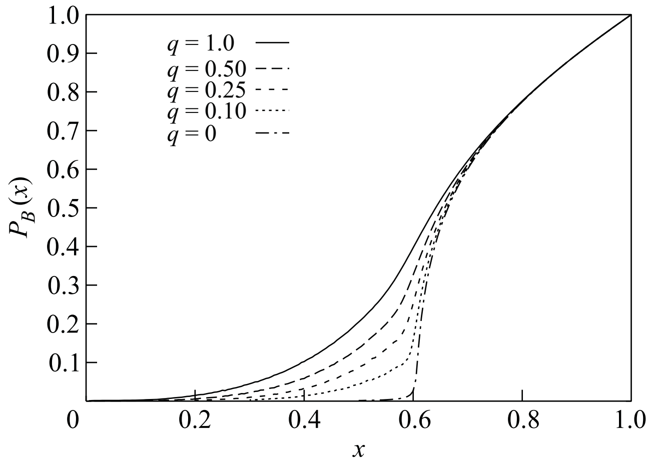

Fig.6. Concentration dependence of the backbone density for a family of BS-SRSP models with different mixing parameters q. The finite density phase transition is absent for all $q > 0$

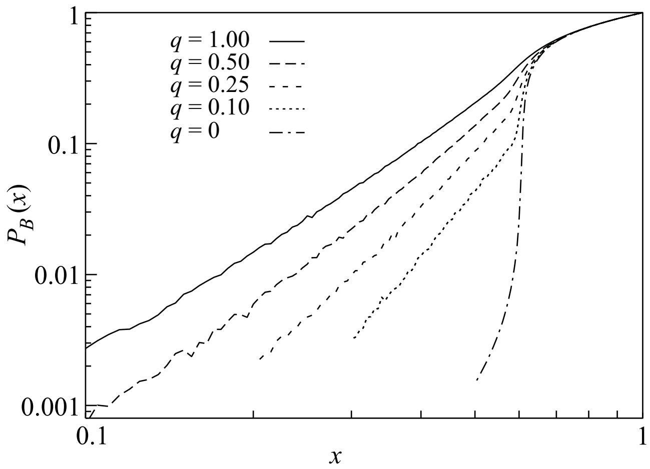

Fig.7. The same as in Fig.6, but in log-log plot. The power-law decay (1) of the backbone density characterized by q-dependent exponent β_B is clearly seen

backbone at all nonzero concentrations. The clusters are especially large in the vicinity of the phase transition. Therefore, one can argue that, when the system approaches the transition, the average number of new bridges per step sooner or later becomes large even for rare sticking events ($q \ll 1$), and further destruction of the backbone eventually slows down. However, we will see in what follows that the large number of new bonds

The backbone density index β_B (see (1)) for the BS-SRSP hybrid models with different mixing parameters q

q	1	0.5	0.25	0.1
β_B	2.85(15)	3.4(1)	4.2(1)	5.2(1)

is not essential for the backbone reinforcement: actually a pair of new bonds on the opposite sides of the cluster already does the job, since it establishes a new long path that crosses the cluster and connects two opposite shores of the mainland.

To demonstrate this we consider the simplest model with moderate backbone reinforcement: a modified variant of SRBP with artificial "two-point sticking". The modification concerns only the repair procedure which is launched after a detachment of a finite cluster. While in the standard SRBP model it was always the regeneration of the bond just removed, in the modified SRBP(2) this procedure is branched:

- if the previous step involved the reparation procedure, then the standard bond regeneration (as in pure SRBP) is always chosen in the present step;
- if the previous step has lead to removal of a bond without a violation of connectivity, then with probability $1 - k$ standard regeneration takes place, while with probability k the "two-point sticking event" occurs: *two* randomly chosen bonds establishing contact of the cluster with the mainland are restored (see Fig.8).

Simulation of the SRBP(2) model shows (Fig.9) that the phase transition is smeared and the backbone exists at all accessible concentrations of bonds $p > p_{\rm tree}$ ($p_{\rm tree} = 1/2$ for the square lattice (see [4]) for all $k > 0$. It makes one assume that the "geometric resonance" effect of the lattice BS model is not essential for the suppression of the topological phase transition, and that the BS model is not pathological and may be trusted in this respect. It can not be excluded that physically reasonable modifications of the BS model exist with reinforcement effect too weak to destroy the finite concentration phase transition. Presently we are studying several candidates for such behavior, but, anyway, we believe that absence of the phase transition is typical for models with backbone reinforcement.

There is an apparent relation between the BS model and conventional diffusion-limited cluster-cluster aggregation (DLCA) (see [2, 9]). Namely, these two models can be viewed as two opposite limits of one generalized model, in which the pore-former particles, randomly distributed in a mixture with matrix grains (the latter having concentration x), are burned at finite rate Γ. The arising free clusters move with finite velocity v (or with finite diffusion coefficient, in the diffusional case). Then the case of relatively slow burning (small Γ) is obviously equivalent to the BS model, while the case of fast burning (large Γ) is described by the DLCA. Indeed,

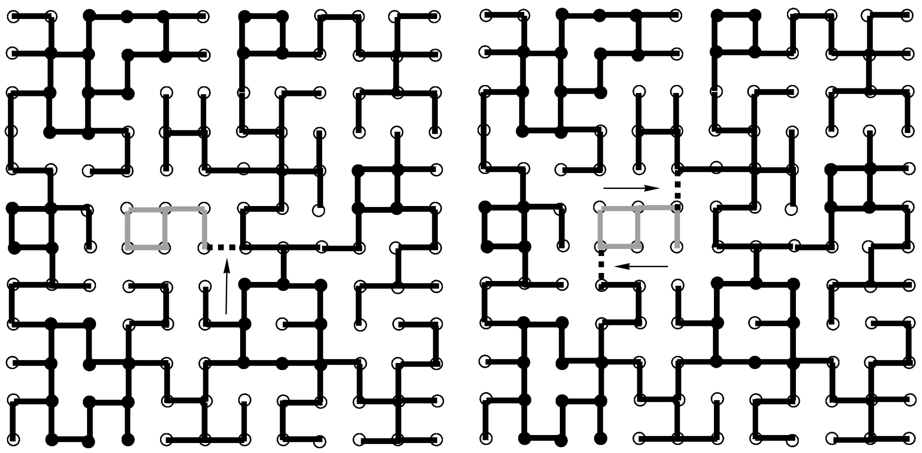

Fig.8. A two-point sticking event in the SRBP(2) model. Left panel: the dashed bond (indicated by arrow) is removed and a finite cluster (shown grey) is created. Right panel: The finite cluster is reconnected to the mainland by restoring two bonds (dashed)

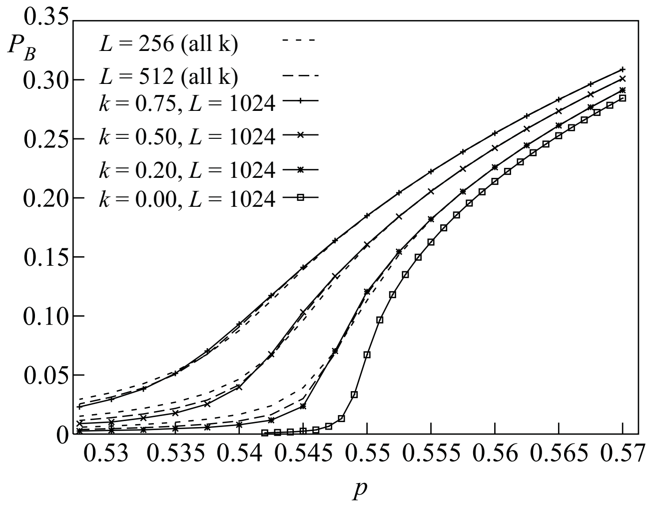

Fig.9. Concentration dependence of the backbone density for the family of modified SRBP(2) models with artificial two-point sticking. The upper three bundles of curves correspond to three different values of the sticking probability k; different curves in each bundle were obtained for different systems sizes L. The lower curve (at $k = 0$) corresponds to pure SRBP model with the phase transition

for large Γ in the initial (fast) stage of the process all the pore-former grains are burned without any considerable motion of emerging clusters. If $x < x_{\rm perc}$, then the infinite cluster is destroyed in the course of burning: the system is "dissolved". On the time-scale $t_b \sim \Gamma^{-1}$ the pore-former is exhausted, and the burning process practically stops, leaving behind a gas of disconnected clusters (in the most interesting case $x \ll 1$ the majority of these clusters are solitary grains). Then the second (slow) stage of the process–the aggregation–begins. It goes exactly along the lines of the DLCA scenario (see [9–14]). At first small clusters stick together eventually forming large fractal flocks (flocculation). At certain "gelation time" $t_g \propto v^{-1}$ the flocks become so large that they pack the entire volume of the system and an infinite cluster arises again in a percolation-type manner. The size of critical flocks at the gelation point is $\xi_F \sim x^{-\nu_F}$, the index $\nu_F = 1/(D - D_F)$ being related to the fractal dimension D_F of the flocks. At the last stage of the process residual free flocks stick to the infinite cluster and finally the system becomes a single-cluster one. On scale $r \gg \xi_F$ the final infinite cluster is practically homogeneous, while for $r \ll \xi_F$ it is a fractal with the same properties, as a solitary critical flock.

It would be extremely interesting to find out if the properties of the final single-cluster state in two limiting cases of slow and fast burning are similar or different. We are planning to answer this question soon.

In conclusion, we have considered burning and sticking model of a porous material that involves sticking of detached clusters to the mainland, and its modifications. Such sticking normally leads to establishing many contacts (at least two) between the cluster and the mainland, which dramatically increases the number of independent paths in the infinite cluster, and therefore leads to backbone reinforcement. The latter effect is manifested in the absence of the topological phase transition (the latter is present in all models without reinforcement). The backbone persists up to $x = 0$, and the system, strictly speaking, remains in the net-like phase at all $x > 0$. At low x, however, the backbone is very loose and feeble, its density obeys the power law (1) with non-universal exponent depending on parameters of the model. The conductivity of the system is extremely poor at low x (though finite, in contrast with the tree-like phase). The backbone has almost single-wired structure with characteristic size of loops ξ_B, which is much larger than ξ_D—the characteristic spatial scale for the density correlations in the entire system. It means that the macroscopic pores in the backbone are filled with almost homogeneous tree-like stuff. A detailed study of the low density state will be presented elsewhere. We have discussed the role of parasitic "geometric resonance" which presumably leads to an overestimation of the backbone reinforcement in the BS model and have demonstrated its irrelevance.

So, we believe that no phase transition occurs in naturally defined models with backbone reinforcement. The simulations of the present paper were performed for the two-dimensional square lattice, but our preliminary results make us expect that the behavior of three-dimensional systems is similar.

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