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Size Dependence of Self-Diffusion in the Hard-square Lattice Gas

J. Jäckle,[1] K. Froböse,[1] and D. Knödler[1]

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A striking size dependence of the mean-square displacement of diffusing particles in the two-dimensional lattice gas of hard squares has been observed by Monte Carlo simulation. It is shown that the size effect is due to the formation of a stable cage structure in small lattices when the particle concentration is high. The formation of cages is governed by a new type of percolation problem related to bootstrap percolation.

KEY WORDS: Lattice gas; self-diffusion; size effect; bootstrap percolation; Monte Carlo simulation.

1. INTRODUCTION

It has been shown in a previous publication[(1)] that the hard-square lattice gas with Kawasaki diffusion dynamics at higher concentrations has dynamical properties which are qualitatively similar to those of undercooled liquids near the glass transition. The extreme slowing down with increasing concentration and the apparent absence of a sharp blocking transition for the self-diffusion in this model correspond to the observed nearly unlimited increase of viscosity and relaxation time and the rounding of the freezing transition in undercooled liquids.[(2)] Moreover, the importance of geometrical constraints makes the hard-square lattice gas a model for highly cooperative dynamics, a concept which so far has been described mainly on intuitive and phenomenological grounds.[(3,4)] In this paper, we show how such cooperativity causes a striking size dependence of self-diffusion, as studied by Monte Carlo simulation.

The hard-square lattice gas is defined by the rule that not only the single sites, but also nearest-neighbor pairs of sites of a square lattice may

[1] Fakultät für Physik, Universität Konstanz, D-7750 Konstanz, Germany.

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be occupied by at most one particle. The second restriction simulates a square-shaped hard core of the particles. As a consequence, the maximum concentration is $c_{max} = 0.5$. At this concentration all the particles are located on one of the two possible sublattices in a checkerboardlike arrangement. (There is an order–disorder phase transition at $c = 0.37$.) The particles are allowed to jump to nearest-neighbor sites. However, a particle can jump only if the occupation rule is also fulfilled after the jump. This implies that three nearest-neighbor sites to the destination site must be empty. If particles happen to be aligned on a diagonal of the lattice without gaps, then all the particles within such a chain block each other mutually. Only the particles at the ends may move if they are not hindered by other particles. Moreover, if such diagonal lines having no mobile particle at the ends are arranged in such a way that they form closed rectangles, they remain stable under the diffusion process. Thus, all the particles enclosed by the rectangles cannot escape from such "cages", and the diffusion is blocked as long as a cage exists. In lattices of finite size, cages may be indefinitely stable. The probability for the existence of a stable cage structure increases with increasing particle concentration, and decreases with increasing system size.

The paper is organized as follows: After reviewing the data on self-diffusion from ref. 1, the results on the size effect are presented in Section 3. In Section 5 the origin of the size effect is explained in terms of cage percolation, which is described in Section 4. A rigorous proof is given in the Appendix that for this type of percolation problem no threshold at an intermediate concentration exists.

2. SELF-DIFFUSION IN BULK

In Fig. 1 the coefficient of self-diffusion in bulk is plotted for higher densities as a function of concentration. (Since nearest neighbors are forbidden, the highest possible concentration of particles on the square lattice is $c = 0.5$.) The coefficient of self-diffusion is obtained from the linear portion of the mean-square displacement curves calculated in ref. 1. The data extend to a maximum concentration of $c = 0.415$ only, since for higher concentrations bulk properties are not obtained for our lattice size of 128×128. As shown in the figure, for concentrations ranging from $c = 0.35$ to this maximum concentration, the data follow the formula

$$D_s(c) \propto \exp\left(-\frac{a}{0.5 - c}\right) \tag{1}$$

with $a = 1.03 \pm 0.03$. Our result is reminiscent of Doolittle's formula[5] for the density dependence of the fluidity (i.e., inverse of the viscosity) of

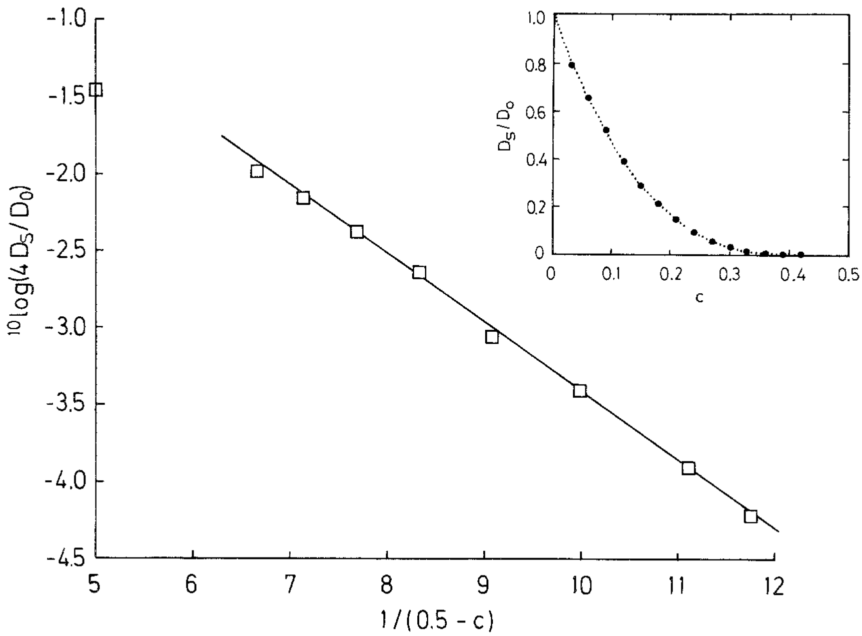

Fig. 1. Concentration dependence of the self-diffusion coefficient D_S in bulk for $c \geqslant 0.3$. Inset: Linear plot including low concentrations. D_0 is the free-particle diffusion constant.

polymers and might suggest that the self-diffusion in the hard-square lattice gas can be explained using the free-volume concept.[6] Indeed, with the simplest assumption that the amount of free volume per site is given by $0.5 - c$ (which is the concentration of holes in the most densely packed configurations), the free-volume idea leads to the functional form of Eq. (1).

In free-volume theory the only characteristic length is the average distance between the units of free volume which are required for molecular mobility. In our case this length would be $d = (0.5 - c)^{-1/2}$. Accordingly, one would expect the self-diffusion in the hard-square lattice gas to become size dependent only when d is of the order of the linear dimension L of the lattice. Even for a relatively small lattice with $L = 32$ this condition is fulfilled only at very high concentration ($d = 32$ at $c = 0.499$). Therefore, the strong size dependence of self-diffusion at much lower concentrations reported below must be related to a different characteristic length which is much longer. Arguments will be given that this length arises from a new type of percolation problem ("rectangular-cluster percolation") which determines whether a stable cage structure exists in a finite lattice.

We note that a similar situation occurs for the two-spin-facilitated kinetic Ising model.[7,8] In this model the spin-flip kinetics is restricted by the rule that (on the square lattice) only spins with at least two up-spin nearest neighbors are allowed to flip. According to Fredrickson,[9] the dependence of the average spin relaxation rate on the up-spin concentration can be fitted by Adam and Gibbs free-entropy theory.[3,2] However, the characteristic length of the Adam–Gibbs theory defined by

$$S_c(d) = k_B \tag{2}$$

where S_c is the configurational entropy in a system of linear dimension d, again is very small except for very low up-spin concentrations and does not explain the size dependence of the spin relaxation rate studied by Nakanishi and Takano.[10] According to these latter authors, the observed size effect is related to the correlation length of a bootstrap percolation problem (with $m = 3$; see refs. 11–13).

3. THE SIZE EFFECT

Figure 2 shows the mean-square displacement $\langle (\Delta \mathbf{r})^2 \rangle_t$ in lattices of four different sizes for times up to 8×10^5 MCS/particle. The concentration is $c = 0.415$. An enormous size dependence is observed. At $t = 2000$ MCS/particle, e.g., the mean-square displacement in the small 16×16 lattice amounts to only 3.5% of that found in the lattice of size 128×128. This size effect is so surprising since it occurs at times at which

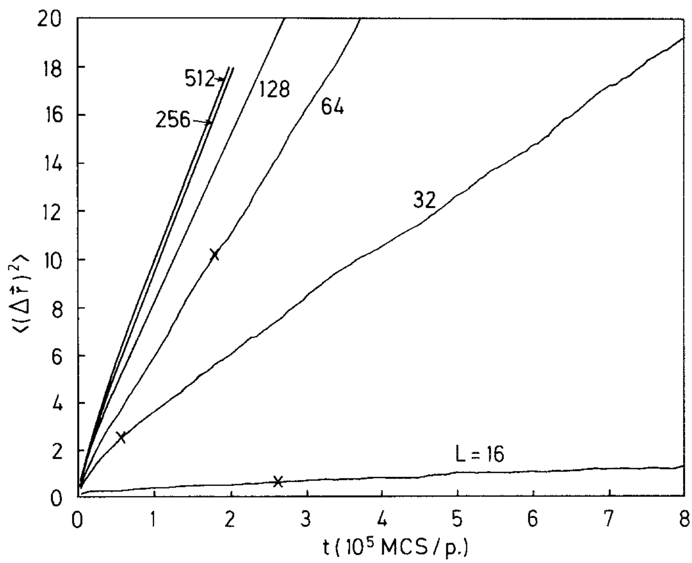

Fig. 2. Lattice size dependence of the mean-square displacement versus time ($c = 0.415$).

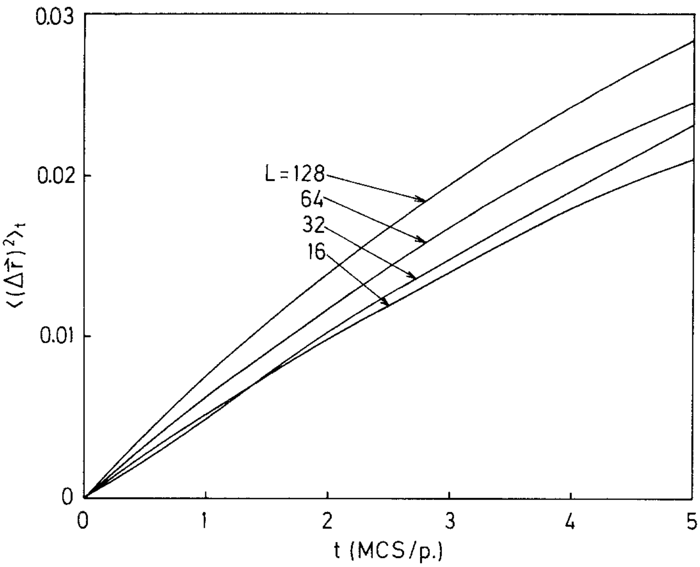

Fig. 3. Size dependence of mean-square displacement at very short times ($c = 0.415$).

the particles have traveled only over a short distance compared with the linear dimensions L of the lattices. On three curves in Fig. 2 the points are marked where the mean displacement is only 1/20 of L. As shown in Fig. 3, the size dependence even persists at the shortest times of the order of 1 MCS/particle.

In very general terms, the fact that the particles "feel" the presence of the boundaries long before having traveled over distances comparable to the lattice size may be interpreted as a striking manifestation of "cooperativity." Apparently a strong correlation between particle motions must exist in regions extending over the entire lattice. The concrete mechanism by which the size effect occurs is suggested by the analysis of the geometrical constraints controlling diffusion in the hard-square lattice gas: In lattices of finite size the diffusing particles may be locked in cages formed by other particles.[1] Since particles forming the cages block each other mutually, perfect cages are infinitely stable. The probability for the existence of stable cages increases with concentration, but decreases with increasing size of the lattice. We propose that the size effect observed in the self-diffusion results from the size dependence of the probability for the existence of a stable cage structure.

We now mention some details of our Monte Carlo calculations. The curves for the mean-square displacement were obtained by averaging over different runs which start from different initial configurations. The number of runs averaged over was 7 for $L = 512$, 30 for $L = 256$, 90 for $L = 64$ and 128, and higher for smaller lattice sizes. The initial configurations were prepared as described in ref. 1. Before the displacements of the particles were recorded, a period of 50,000 MCS/particle was allowed for thermalization. We tested whether our results depend on the length of the thermalization period. For our highest concentration $c = 0.415$ we found that in a lattice of size $L = 512$ the mean-square displacements are higher by about 4% if the thermalization period is extended to 150,000 MCS/p. An increase to 250 000 MCS/p, however, did not change the results further. Because of the very slow thermalization at $c = 0.415$, therefore, our Monte Carlo data are accurate only to within about 5%. At lower concentrations there is no problem with the length of the thermalization period.

4. PERCOLATION OF CAGES

The problem of calculating the probability for the existence of a stable cage structure is simplified by the fact that only configurations with particles on one particular sublattice of the square lattice need to be considered. Using this fact, the cage problem can be formulated as a new type of percolation problem for this sublattice, which we termed "rectangular-cluster percolation." It is assumed that all particles may be placed randomly on this sublattice.[1] The rectangular clusters are defined as the smallest rectangles in which the clusters formed by nearest neighbors can be embedded. It has been shown[14] that the rectangular-cluster percolation problem defines a cellular automaton, in which all particles with a certain neighborhood of vacancies are successively removed. The condition for removal is that three neighboring vacant sites and the site occupied by the particle are the corners of a unit square of the square lattice. Accordingly, in the terminology of Adler *et al.*,[15] the rectangular-cluster percolation problem can be classified as a diffusion percolation problem of type $c3n$. The desired probability in the cage problem is the complement of the probability for the percolation of rectangular clusters covering the holes on the partially filled sublattice.[1] The hole concentration relative to the sublattice is given by $c_h = 1 - 2c$, where c is the particle concentration on the full square lattice. In the Appendix we prove that for any nonzero value of c_h the rectangular clusters percolate in the thermodynamic limit $L \to \infty$. For any particle concentration $c < 0.5$, therefore, in sufficiently large lattices at most an incomplete and unstable local cage structure can exist. The dependence of the probability to percolate p of the rectangular clusters on L defines a characteristic length ξ_P by

$$p(c_h, L = \xi_P) = P \tag{3}$$

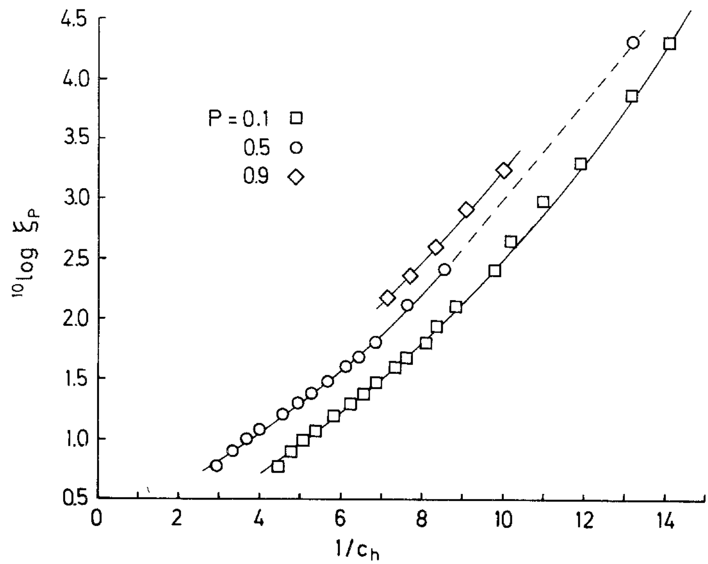

Fig. 4. Characteristic lengths of the rectangular-cluster percolation problem as a function of hole concentration $c_h = 1 - 2c$. Data are shown as points. Lines are only guides to the eye.

Figure 4 shows the concentration dependence of this length obtained for $P = 0.1$, 0.5, and 0.9, respectively. Apparently, the data are compatible with finite-size scaling.[16]

We note that the slight bending of the curve for $P = 0.1$ points to a divergence of the characteristic length at a finite hole concentration $c_h = 0.04$.[14] This result, which is in conflict with the proven absence of a finite percolation threshold, implies that in the rectangular-cluster percolation problem asymptotic behavior is not reached even for L as large as 20,000. It is important for the comparison of the hard-square lattice gas model with the two-spin facilitated kinetic Ising model that this bending is absent in the corresponding curve for the $m = 3$ bootstrap percolation problem.[10] One reason for this difference is that in the $m = 3$ bootstrap percolation problem two voids of rectangular shape must be separated by *two* fully occupied lines in order to be stable, whereas in the $c3n$ diffusion percolation problem a *single* line is sufficient.

5. EXPLANATION OF THE SIZE EFFECT

The rectangular-cluster percolation problem underlying the diffusion of hard squares on a finite square lattice introduces a characteristic length $\xi \equiv \xi_{0.5}$ which is large compared with the lattice spacing already at moderate concentrations c (cf. Fig. 4). It is easy to see that this length controls the asymptotic behavior of the mean-square displacement at long times. Since in samples with a stable cage structure the diffusing particles are forever trapped in cages, only samples in which the cages are unstable and percolate contribute to the asymptotic linear increase of the mean-square displacement with time. The mean-square displacement at long times may therefore be expected to be proportional to the probability to percolate $p(c_h, L)$ of the rectangular clusters, which is a function of ξ/L according to finite-size scaling.

We suggest that ξ/L also controls the size effect observed at intermediate and short times which was described above. The evidence for our suggestion is shown in Fig. 5. Here the size dependence of the mean-square displacement at different times ($t = 10^2$, 10^3, 10^5 MCS/particle) is compared with that of the probability for rectangular-cluster percolation, viz. for absence of stable cages. For each time the mean-square displacements are normalized relative to the value obtained in the largest lattice ($L = 512$). The particle concentration is $c = 0.415$. The essential result of Fig. 5 is that the reduction with decreasing lattice size of both the mean-square displacements and the probability to percolate of the rectangular clusters occur within the same range of L values. However, even for the longest

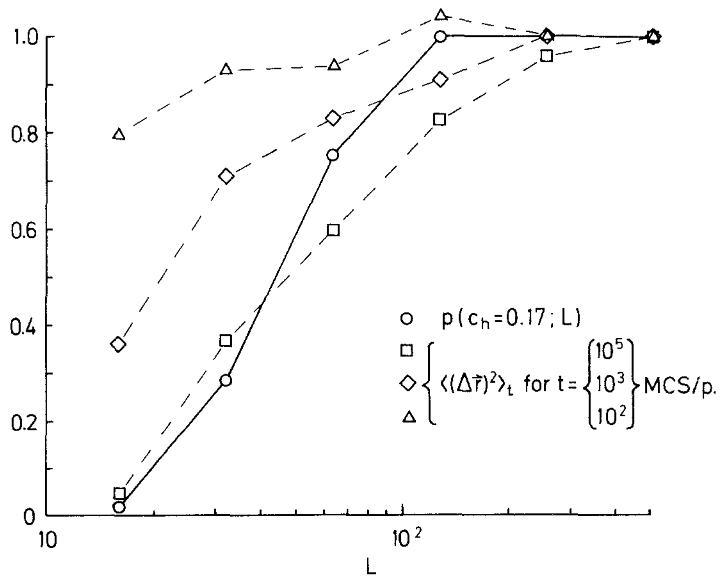

Fig. 5. Comparison of size dependence of mean-square displacements at different times and of the probability for rectangular-cluster percolation ($c = 0.415$). For each time the mean-square displacements are normalized relative to the value for $L = 512$.

time ($t = 10^5$ MCS/p) the curve for the mean-square displacement is not strictly proportional to that for the probability to percolate. The mean-square displacement starts to decrease markedly from the bulk value already between $L = 256$ and $L = 128$, where the probability to percolate still is very close to one. Strict proportionality of the two curves is expected to hold only asymptotically.

One might hope to get rid of the size effect by using only data from percolating samples, i.e., by discarding all samples with a stable cage structure. In Fig. 6 mean-square displacement curves derived from percolating samples only are shown together with those obtained by averaging over all samples. The size-dependent *reduction* of the mean-square displacement with decreasing L goes away, but now a size dependence of the opposite sign appears! Apparently, by throwing out for small lattice size all samples with a cage structure, one also eliminates some of the kinetic restrictions present in large percolating samples. It does not seem to be possible to avoid a size effect in small lattices by using an ensemble of percolating samples only. Despite this puzzling result, however, there is no doubt that the formation of stable cages, which is controlled by the rectangular-cluster percolation problem, is the principal cause for the observed size dependence of self-diffusion in the hard-square lattice gas.

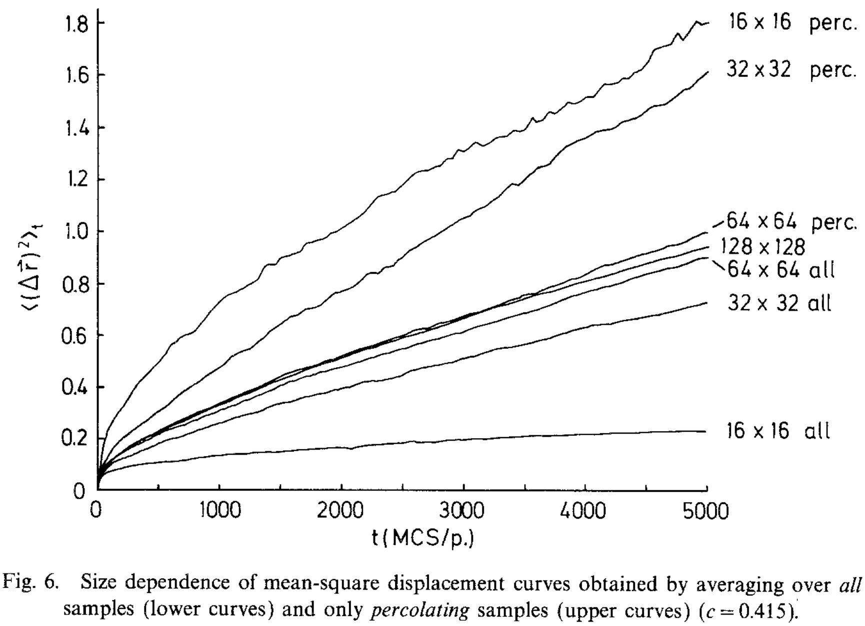

Fig. 6. Size dependence of mean-square displacement curves obtained by averaging over *all* samples (lower curves) and only *percolating* samples (upper curves) ($c = 0.415$).

APPENDIX. PROOF OF ABSENCE OF A THRESHOLD FOR RECTANGULAR-CLUSTER PERCOLATION ON THE SQUARE LATTICE

The elementary proof presented in ref. 1 is formulated with mathematical rigor, avoiding the approximate solution of a recurrence relation. Using a growth-of-squares process, a lower bound for the probability to percolate is calculated and shown to converge to unity in the thermodynamic limit $L \to \infty$. This result is valid for any nonzero concentration.

We mention that for the related problem of bootstrap percolation on a square lattice with characteristic number $m = 3$, van Enter has given a proof of the absence of a threshold at nonzero hole concentrations.[17] With a slight modification, his proof can be extended to the case of rectangular-cluster percolation.[14] Compared with van Enter's proof, which is based on a theorem of ergodic theory, the proof presented here is direct and more transparent.

We first consider a finite lattice of size $L \times L$. In the context of diffusion in the hard-square lattice gas we speak of holes which randomly occupy the sites of the lattice with probability c_h. Periodic boundary conditions are assumed. We divide the lattice into L subsystems of size $\sqrt{L} \times \sqrt{L}$ and grow quadratic clusters starting from the centers of these subsystems.[1] The growth process is described by an integer variable l between 1 and $\sqrt{L}$. The probability that a quadratic cluster of size $l \times l$ grows around a particular site is denoted by $p_l(c_h)$. The probability that a subsystem is completely covered by the growth process is given by $p_{\sqrt{L}}(c_h)$. A quadratic cluster of size $l \times l$ grows by one adjacent line in all four directions if in each of these lines there is at least one hole. According to this growth rule, the probabilities $p_l(c_h)$ obey the recurrence relation

$$p_{l+2}(c_h) = p_l(c_h) \cdot [1 - (1 - c_h)^l]^4 \tag{A1}$$

where $p_1(c_h) = c_h$. Since the L subsystems do not overlap, the growth processes within them are statistically independent. Therefore the probability that at least in one of them a cluster of size $\sqrt{L} \times \sqrt{L}$ is grown is given by

$$1 - [1 - p_{\sqrt{L}}(c_h)]^L \tag{A2}$$

Next, one of the subsystems which are completely covered by a square cluster is placed in the center of the $L \times L$ system, and the growth-of-squares process is continued around this $\sqrt{L} \times \sqrt{L}$ cluster. The probability that the process does not stop before the whole $L \times L$ lattice is covered amounts to

$$\frac{p_L(c_h)}{p_{\sqrt{L}}(c_h)} \tag{A3}$$

Combining expressions (A2) and (A3), we find the probability for obtaining a covering cluster of size $L \times L$ to be

$$\{1-[1-p_{\sqrt{L}}(c_h)]^L\} \cdot \frac{p_L(c_h)}{p_{\sqrt{L}}(c_h)} \tag{A4}$$

Since the growth-of-squares process neglects the occurrence of nonquadratic clusters and the growth by overlap of clusters, (A4) represents a lower bound to the probability to percolate for rectangular clusters in an $L \times L$ lattice. To prove that this lower bound converges to unity in the thermodynamic limit, it is sufficient to show that $p_l(c_h)$ converges to a nonzero limit $p_\infty(c_h)$ for $l \to \infty$. Since $p_l(c_h)$ decreases monotonically with increasing l, a lower bound to (A4) is

$$\{1-[1-p_\infty(c_h)]^L\} \cdot \frac{p_L(c_h)}{p_{\sqrt{L}}(c_h)} \tag{A5}$$

which converges to unity for $L \to \infty$ since the convergence of $p_l(c_h)$ implies that $p_L(c_h)/p_{\sqrt{L}}(c_h) \to 1$ for $L \to \infty$. The convergence of $p_l(c_h)$ to a nonzero limit is proved using the ratio test for $\ln p_l(c_h)$. From the recurrence relation (A1) we derive the infinite series

$$\ln p_\infty(c_h) = \ln p_1 + 4 \sum_{l=1}^{\infty} \ln[1-(1-c_h)^{2l-1}] \tag{A6}$$

Because of

$$\frac{\ln[1-(1-c_h)^{2l+1}]}{\ln[1-(1-c_h)^{2l-1}]} \xrightarrow{l \to \infty} (1-c_h)^2 < 1 \qquad \text{for} \quad c_h > 0 \tag{A7}$$

the series converges for any nonzero hole concentration c_h by the ratio test. Obviously, $\ln p_\infty$ is negative, so that

$$0 < p_\infty(c_h) < 1 \tag{A8}$$

holds. This completes the proof that the probability to percolate for rectangular clusters is unity in the thermodynamic limit for arbitrary finite (hole) concentration.

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