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Exact relations between kinetic gelation and percolation

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Abstract. An exact relation between one of the recently introduced models for kinetic gelation and random percolation is displayed. This explains the frequently observed identity between the exponents of the two models. Moreover, it strongly suggests that any further universal properties of percolation are also shared by kinetic gelation. In particular, a rigorous inequality due to van den Berg and Kesten can be used to display an inconsistency between the observed values of the exponents β and ν and the observed value of the fractal dimension of the backbone in kinetic gelation. The more complex issue of the observed variation of the amplitude ratio cannot be easily resolved, however. Should the observed discrepancies be real, they would, according to our results, indicate that the amplitude ratio can indeed vary depending upon the underlying lattice structure.

1. Introduction

A widely used model for the understanding of gelation is the percolation model: it is assumed that, during the polymerisation process, bonds form at random between polyfunctional units until an infinite network is formed. This clearly represents a rather strongly idealised view of the facts. In particular, in the case of addition polymerisation, the neglect of kinetic effects has been felt to be of considerable importance. For this reason, Manneville and de Sèze [1] introduced a model—now generally known as kinetic gelation—to introduce the non-equilibrium features lacking in ordinary percolation.

This model—to be described in greater detail in the next section—has been the object of considerable study in recent years. In a pioneering study, Herrmann, Landau and Stauffer [2] found that the fractal dimension of the clusters thus generated was equal to that of ordinary percolation clusters, but that another supposedly universal quantity, the amplitude ratio for the susceptibility, was markedly different from its ordinary percolation value. In a broad overview of all the variants of the model (which are quite numerous indeed) Pandey [3] confirmed the deviation from the percolation value. In two dimensions, a more complicated situation arises, as trapping and annihilation now become of greater importance, due to the compactness of random walks in two dimensions. Nevertheless, the identity between the exponents of kinetic gelation and percolation has been confirmed [4]. With additional research, further anomalies were noted: first, the cluster size distribution was found to be non-monotonic [5] in stark contrast to ordinary lattice percolation. Instead, oscillations were observed which made impossible the fitting of the cluster size distribution by a law of the form

$$n_s(p) \simeq q_0 s^{-\tau} f(s/|p-p_c|^{\sigma}) \tag{1.1}$$

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in the way that is ordinary used in the scaling theory of percolation. Rather, this form has to be multiplied by a periodic function of s. Careful numerical work appears to indicate that these oscillations die out quite slowly, if indeed they die out at all. However, later work [6] showed that this alone could not explain the change in the amplitude ratio. Only a change in the (supposedly universal) scaling function $f(x)$ could accomplish this. Moreover, studies of the fractal dimension of the backbone of these clusters showed numerically results distinctly different from those obtained in ordinary percolation [7]. However, the exponents characterising the shortest path on a cluster as well as that characterising diffusion appear to be the same [8, 9]. The latter is particularly surprising in view of the connection between diffusion and conductivity via the Einstein relation. Thus, the identity of the diffusion exponent means that the conductivity exponent is the same. Since conductivity is limited to the backbone, however, it would appear that a large change in the backbone dimension should also manifest itself in the exponent for the conductivity. That this does not appear to be the case is therefore a rather unexpected result.

The purpose of this paper is to show an exact relationship between kinetic gelation in one of its simplest variants—the so-called mole's labyrinth introduced by Herrmann [8]—and a random percolation model on a rather complex lattice. This would indicate, therefore, that one does not expect any differences between the mole's labyrinth and percolation, other than those ordinarily associated with the lattice. This would appear to rule out any of the discrepancies observed above. Indeed, as we shall see, the values given for the backbone dimension in [7] are incompatible with the values observed for β and ν. In this case, it is fairly straightforward to identify the reason for a very long crossover behaviour. The issue of the amplitude ratio for the susceptibility, however, is somewhat more mysterious.

The organisation of this paper is as follows: in section 2, we define the model and all the various parameters that have been varied. In section 3, we give the equivalence between the mole's labyrinth and random percolation. We further discuss the effects of the different variants. As will become clear, the effect appears to be—with one possible exception—the introduction of short-range correlations into the model. These should not change the universality class, a fact confirmed by the numerical finding that the other kinetic gelation models show the same kind of behaviour evidenced by the mole's labyrinth. In section 4 we discuss the apparent conflict between the exact results obtained and the numerical data. In particular, we show that the reported dimension of the backbone is inconsistent with the data on the fractal dimension of the cluster itself, using a rigorous result due to van den Berg and Kesten.

2. The model

Kinetic gelation has been defined in many subtly different ways. For this purpose, it is probably best to start with the simplest model, the mole's labyrinth, and proceed to introduce the various complications one by one. In this simplest model, one starts with a concentration c_1 of initiators. These are randomly placed on a lattice at time zero. They then proceed to move as a random walk. At each step, a bond is created between the starting site and the ending site. In this model, of course, sites may be connected by multiple bonds, but we shall not assign any particular significance to this fact. As time goes on, the various clusters start to bind among each other, until they form an infinite network, i.e. a gel. As in ordinary percolation, the following

quantities can be defined: $n_s(t)$ as the number of clusters of s sites at time t, $P_\infty(t)$ as the probability of a site belonging to the infinite cluster (or, in more traditional terminology, the gel fraction) and finally $\chi(t)$ defined as the weight-averaged cluster size excluding the infinite cluster. More precisely:

$$\chi(t) = \sum_{s=1}^{\infty}{}' s^2 n_s(t) \tag{2.1}$$

where the prime indicates that only the finite clusters should be summed over. The time at which $\chi(t)$ diverges is called t_c and has been found to be identical to the one beyond which $P_\infty(t)$ becomes different from zero. Defining ε as $|t - t_c|/t_c$, one obtains the following behaviour:

$$\begin{aligned} \chi(t) &\simeq A_- \varepsilon^{-\gamma} \qquad t \leqslant t_c \\ \chi(t) &\simeq A_+ \varepsilon^{-\gamma} \qquad t \geqslant t_c \\ P_\infty(t) &\simeq \varepsilon^{\beta} \qquad t \geqslant t_c. \end{aligned} \tag{2.2}$$

A further exponent ν can be defined from the decay of the connectedness function $g(r)$, which is defined as the probability that two points at a distance r be in the same cluster. This is found to be

$$g(r) \simeq r^{-(d-2)+\eta} \exp(-r/\xi) \tag{2.3}$$

where ξ diverges as $\varepsilon^{-\nu}$. The exponents are therefore quite similar to the ones defined analogously in percolation. Within the error bars, they have usually been found to agree with the accepted values for percolation [2, 8].

This led rather naturally to the question as to whether some other characteristic quantity might not exist that would distinguish between kinetic gelation and percolation. The fractal dimension d_f of the clusters themselves is not enough, since one has the relation [10]

$$d_f = d - \beta/\nu \tag{2.4}$$

and therefore nothing new can be expected from this exponent. Two further quantities, however, usually also thought to be universal [11], have been investigated in this respect: the susceptibility amplitude ratio R defined as A_-/A_+ and the fractal dimension of the cluster backbone d_{BB}, defined as the set of points connected to infinity by two disjoint paths or, equivalently, as the set of self-avoiding paths connecting two widely separated points. Numerically, both of these have been found to differ significantly from their percolation counterparts in three dimensions: while R has a value of approximately 10 in percolation, in kinetic gelation it appears to vary continuously with c_1 eventually settling somewhere around 2 for quite small values of c_1. As for d_{BB}, it appears to be approximately 2.3 as opposed to a value of about 1.8 in percolation. The situation in two dimensions is somewhat more complex and has not, to my knowledge, been explored as fully.

Let us now come back to our original purpose and describe the several variations upon this simplest model. The earliest models are defined as follows: a lattice is given, filled with f-functional units ($f > 2$) and a concentration c_1 of initiators is distributed on the lattice. The initiators then move as follows: at each time step, an initiator is selected at random and moved in any direction. If it meets another initiator, a bond is created by the move but the two annihilate. If it meets an unsaturated f-functional unit, the move is accepted and a bond is created. Otherwise, the move is rejected and

the initiator remains where it was. An initiator wholly surrounded by saturated initiators is said to be *trapped.* In the case where f is odd, trapping can also occur through the impossibility of leaving a saturated f-functional unit.

Clearly, the model just outlined is a far more realistic version of what actually occurs in an addition polymerisation situation. Furthermore, additional variants have been studied, where the reactive units are taken to be a mixture of f- and g-functional units. The case $g=2$ in particular has been the object of considerable study [3]. An additional, also frequently introduced complication is a certain concentration of solvent molecules, i.e. molecules which do not react at all. While all these profoundly affect the phase diagram, however, they do not appear to modify the basic results in any fundamental way.

Summarising, the effects of the various modifications can be characterised as follows:

(i) annihilation: when two initiators meet, they annihilate;

(ii) trapping: under given circumstances, an initiator may not be able to move further;

(iii) disorder: depending upon the specific configuration of f- and g-functional groups in the neighbourhood of a certain initiator, this initiator's possibilities to generate various types of clusters will be affected: the system is therefore, under these circumstances, no longer translation invariant.

Each of these features can be (and has been) introduced independently from the others. Thus trapping can be suppressed by letting f go to infinity. Annihilation can be suppressed by convention and disorder is altogether independent of either.

All these variants may, in some sense, be said to involve only the rules to move the initiators. Others yet concern the way the initiators are introduced into the system: whether suddenly or gradually, whether at random or on a periodic array. We shall consider these modifications separately, as they are of a very different nature from the ones discussed above.

3. The mole's labyrinth

In this section, we wish to display an equivalence between the mole's labyrinth and site percolation on an appropriately chosen lattice. In the mole's labyrinth, we have two parameters determining criticality: c_1 and t. While it has, in previous studies, been found convenient to vary t at fixed c_1, we shall do the opposite: clearly, this does not change anything, apart from the angle at which the phase boundary is crossed. Let us call Λ the d-dimensional lattice on which the system is assumed to be defined. We shall assume the dimensions of Λ to be large but finite and denote them by L. For definiteness' sake as well as to maintain translational invariance, we shall use periodic boundary conditions on Λ. This is not, however, essential to the argument. At fixed t, however, every initiator has performed one of a certain set of random walks on Λ. Let Σ denote the set of all random walks of t steps starting at the origin. To each initiator, therefore, there corresponds an element of Σ. Note that, since t never becomes infinitely large, the set Σ is finite and does not have a diverging number of elements. Let us now define the lattice which will be the crucial construct in what follows: let Γ be defined as the set $\Lambda \times \Sigma$ with the following lattice structure: let us denote elements of Λ be vectors of the form $\boldsymbol{x}$ and elements of Σ by Greek letters. We say that two elements of Γ, $(\boldsymbol{x}_1, \alpha_1)$ and $(\boldsymbol{x}_2, \alpha_2)$, are connected by a bond if the random walk α_1

starting at x_1 intersects the walk α_2 starting at x_2. Since, as pointed out above, Σ is a finite set as opposed to Λ, the dimensions of which go to infinity, the lattice Γ is merely an ordinary three-dimensional lattice with connections beyond nearest neighbour. In the following, we shall denote elements of Γ by Greek vectors, say ξ.

From the preceding construction, however, one sees that kinetic gelation at time t and concentration c_1 is obtained by randomly placing initiators on the lattice Γ. Those initiators belonging to the same cluster are connected by construction. The other points, however, are, in a sense, invisible. Thus, this procedure does not generate the 'full' clusters but only a 'skeleton' consisting of those initiators that belong to the clusters at the position they occupied initially. This means that the mass of the clusters we have defined is not the same as the mass of the clusters observed in the original algorithm. To see that this difference is not essential, however, we proceed as follows: to each bond connecting two initiators at x_1 and x_2, let us assign as weight the total number of *different* sites on Λ visited by the two random walks connecting them. We can now assign two different masses to every cluster: the first is simply the number of initiators in the cluster, the second is the sum of all the weights of the bonds in the cluster. Clearly, the actual mass is between those two (it is not necessarily equal to the latter, since sites may be visited by three or more walks). By definition, however, the weights of each bond lies between 1 and $2t$, so that the masses of the clusters in the actual model are between the number of initiators and $2t$ times that number.

Thus, for large cluster sizes, no difference is expected between the cluster size distribution of the mole in the labyrinth and that of percolation on the Γ lattice. Further, by universality, no differences are expected in the critical behaviour of the cluster size distribution between various lattices. We will attempt to display reasons for the discrepancy with numerical results later. For the moment, we have shown that the mole's labyrinth and percolation belong to the same universality class just as two versions of the percolation model on two different lattices do. There is one small caveat, however: in the mole's labyrinth, it is usually assumed that no two initiators will originally occupy the same site. This condition is not required in random percolation on the Γ lattice, since we very well may have two points (x, α_1) and (x, α_2) being both occupied. However, it would be easy to relax that condition on the mole's labyrinth. Further, since the most striking discrepancies are observed at rather small c_1 (of the order of 10^{-2}–10^{-4}), it does not appear at all likely that this would change anything. Furthermore, the introduction of such a constraint on percolation on the Γ lattice would, in fact, amount to a short-range correlation to the percolation problem, which is generally assumed not to modify the universality class of percolation.

Essentially the same remarks hold for the manifold variants of kinetic gelation: first they all appear to yield similar discrepancies from percolation as the mole's labyrinth. Second, they can all be accounted for by introducing short-range correlations and possibly disorder in the lattice. Let us consider this in somewhat more detail.

First let us look at trapping. The phenomenon of trapping arises from imposing the constraint that the path of an initiator be self-avoiding. This immediately leads to redefining Σ as the set of all allowable paths of t steps of an initiator in the absence of any others. This accounts for such phenomena as self-trapping and the use of kinetic growth walks [12, 13] instead of random walks for the propagation of the initiators. Trapping, however, has also another aspect, which is somewhat more difficult to handle: an initiator can quite easily be trapped in the cluster generated by another initiator. This cannot, of course, be accounted for merely by redefining Σ. It can, however, be reduced to a short-range correlation on the Γ lattice by the following

considerations: the vector $\xi = (x, \alpha)$ of Γ represents an allowable (i.e. non-self-trapping) walk α starting at x. This walk can only be trapped by other walks $\eta_1, \ldots, \eta_k$ if these walks pass within one lattice spacing of the walk ξ. This means that the walks $\eta_1, \ldots, \eta_k$ are all within one lattice spacing of being nearest neighbours to ξ. Thus, the walks capable of trapping ξ are all in the neighbourhood of ξ itself, so that the walks which ξ intersects in the presence of trapping by other clusters can be determined knowing which of the points one lattice spacing away from a nearest neighbour of ξ are occupied. Thus, ξ is not automatically connected to all of its occupied nearest neighbours, but only to those it encounters before being trapped by one of the walks passing within one lattice spacing of it. Although this may appear to be a fairly long-range effect, this is not the case if it is borne in mind that we are considering a case where the gelation time is not critically large. Note, in particular, that k is bounded from above by the number of points accessible in time t and therefore is not critically large in the thermodynamic limit.

Similarly, annihilation is a restriction on the possible paths in much the same way as is trapping by another initiator. It can therefore be handled in exactly the same manner. Again, for $d > 2$, annihilation becomes less and less likely as c_1 goes to zero. As we have mentioned before, however, this is where the strongest differences between percolation and kinetic gelation appear. For $d = 2$, the issue of annihilation is particularly difficult: since random walks are compact for $d \leqslant 2$, annihilation may become more and more important as c_1 goes to zero. We should not, however, lose sight of the fact that, even in two dimensions, the correlations introduced by annihilation do not extend further than $\sqrt{t}$, so that they are still properly thought of as short range. This is confirmed by the finding [4] that the exponents for percolation and kinetic gelation have compatible values.

As for disorder, such as is introduced by having a random mixture of f- and g-functional units on the lattice, it can be incorporated by using a slightly more complex variation on the Γ lattice: given an initial mixture, the generalised Γ lattice is constructed as follows: to every point x of Λ, assign a set $\Sigma(x)$ denoting all walks of t steps allowable knowing what units surround x. The Γ lattice is then defined as the set of all pairs (x, α), where x belongs to Λ and α to $\Sigma(x)$. The bonds are defined as usual. This lattice is not translation invariant any longer. This should not have any effect on the exponents but there is some evidence that it might have an effect upon the amplitude ratio [14] even in ordinary percolation. However, it should be pointed out that, in kinetic gelation, non-universal amplitude ratios have also been observed under circumstances involving no disorder, such as in the mole's labyrinth.

4. Discrepancies with numerical data

In this section, we make a series of hypothetical claims concerning the possible mechanisms yielding those features of kinetic gelation which are clearly different from percolation. Let us start with the most prominent difference between the cluster size distribution of the mole's labyrinth and that of standard percolation, that is the presence of oscillations of finite frequency in s. These may be supposed to arise from the fact that the growth process of clusters at low c_1 may be separated in two rather distinct stages: in the first, every initiator grows without interacting with the others (the existence of such a stage is a natural consequence of the smallness of c_1), whereas in the second, the clusters thus formed begin to coalesce and form an infinite network over a

comparatively short time span compared with the first stage. Such a picture would explain the oscillations as arising from the fact that the building blocks from which the clusters are made are themselves random walks of a fairly well determined size, so that clusters tend to have masses that are multiples of that characteristic size. Such a picture is, however, rather hypothetical at present and numerical work to confirm or invalidate it would be quite worthwhile. If this picture is indeed correct, the frequency of the oscillations should be proportional to the number of sites in a random walk connecting two typical nearest-neighbour sites. For the mole's labyrinth, this turns out to be

$$\begin{aligned} s^* &\simeq -c_1^{-1}/\ln c_1 \qquad d=2 \\ &\simeq c_1^{-2/3} \qquad d=3. \end{aligned} \tag{4.1}$$

In the case $d=1$ there are no such easily defined oscillations of the cluster size distribution, due to the absence of a non-trivial percolation transition. For $d \geqslant 4$ it is not clear whether the oscillations will subsist, as under these circumstances the above scenario is not self-consistent: indeed, in such high dimensions, it is quite unlikely that two nearest neighbours should coalesce with one another, since random walks are then penetrable. Rather, we should expect that every cluster should coalesce with roughly equal probability with every cluster within its reach. It is then unclear, whether the assumption that the coalescing clusters have a well defined size is still warranted. If they do, this size will simply be proportional to t_c, which we proceed to estimate.

The scaling of the critical time t_c as a function of the concentration c_1 can be obtained as follows. In two and three dimensions, the critical time is expected to scale as the square of the typical nearest-neighbour distance, that is, as $c_1^{-2/d}$. This is due to the fact that every initiator is likely to react with one of its nearest neighbours. For $d \geqslant 4$ on the other hand, the following argument gives an indication of what is to be expected: after a time t, a given initiator has generated a cluster of radius $\sqrt{t}$ and is therefore capable of reaching all the clusters within that distance. The number of such clusters is $c_1 t^{d/2}$. On the other hand, the probability that two such clusters meet is of the order $t^{2-d/2}$. Therefore, the probability that the cluster has coalesced with another becomes of the order of unity when $c_1 t^{d/2} \simeq t^{2-d/2}$ or, in other words, the time after which one expects coalescence is of the order of $c_1^{1/(2-d)}$.

Note in passing that a similar reasoning could be made for a ballistic version of the mole's labyrinth model, where the initiators move in straight lines with random directions. The advantage of such a model is that the dimension above which straight lines become transparent to one another is two, so that a three-dimensional simulation would allow one to probe this regime and verify, for example, whether the critical time does indeed scale as $c_1^{1/(2-2d)}$, where the above reasoning has been adapted to the ballistic case. Obviously in this particular example, the oscillations are not suppressed above the dimension where the trajectories become transparent.

As a summary, it would appear that the oscillations observed in the cluster size distribution of kinetic gelation are due to the different way the mass of a cluster is calculated: in the model on the Γ lattice, the mass of a cluster is reckoned by the number of initiators that participated in its formation. In ordinary kinetic gelation, the sites bound to the cluster by the initiator are also considered. The explanation for the oscillation then lies in the fact that every initiator contributes in general a fairly well defined, though no doubt fluctuating number of particles to the whole cluster. Thus the cluster masses tend to come in multiples of the typical size that a cluster

generated by an initiator reaches before coalescence. This is confirmed by the fact [15] that the oscillations disappear if the initiators are introduced gradually instead of all at the same time. This is readily accounted for by our picture, since at the critical time t_c there will be clusters of all possible sizes, so that it is not possible to talk of a well defined typical size of the clusters coalescing at criticality.

As has been shown in [6], however, the mere presence of oscillations is not enough to explain the difference in amplitude ratio. To this end it would be necessary to assume that the scaling function as defined in (1.1) be different for the two models. It is generally accepted, however, that such functions are indeed universal, at least to the extent of being lattice-independent. The observed lower values of R are therefore presumably the result of crossover behaviour. There does not, however, appear to be a satisfactory explanation for such a crossover. At first sight, it might appear that we have a rather long-range percolation problem, since the bonds on the Γ lattice can be quite long, in terms of the lattice spacing, if c_1 is small. This would imply that one has a long mean-field crossover behaviour until finally the correct behaviour is attained. This might in turn be thought to explain the lowering of the amplitude ratio from its three-dimensional value, since in mean-field it is equal to one. This is misleading, however. The crucial point in this respect is that the spacing in the original lattice Λ is not at all a relevant length scale, except insofar as it sets a 'capture radius': two clusters react when they come closer to each other than the lattice spacing. However, as long as random walks remain opaque to each other, i.e. for $d < 4$, capture will occur irrespectively of the value of the capture radius. This is most easily seen by letting this spacing go to zero, keeping the original distribution of initiators fixed. Rescaling time appropriately, one is led to a model of kinetic gelation involving continuous Brownian motion. For $d < 4$, however, crossing of two Brownian paths will still occur with probability one within finite time. Thus we see that the range of the links should not be measured in units of the lattice spacing and are therefore not related to c_1. Thus the range does not, in fact, go to infinity as $c_1 \to 0$, unless $d \geqslant 4$. A more correct way of posing the problem is to ask about the number of initiators within a distance $\sqrt{t}$ of a given initiator at the critical time. If this number is very large, one expects a long mean-field crossover behaviour. This will presumably occur for $c_1 \to 0$ in dimensions higher than four. It will never, however, occur in lower dimensions, and indeed, for the exponents, no long mean-field crossover behaviour has ever been reported for three-dimensional systems. This shows that in the limit $c_1 \to 0$, the dimension four plays an important role, due to the fact that random walks become transparent above it [8]. This should not, however, be confused with the critical dimension of the model, where the exponents assume their mean-field value. Due to the equivalence of the mole's labyrinth with percolation, this dimension is six. Again, the distinction becomes clearer in the ballistic case, since there the trajectories already become transparent in three dimensions.

Some light was shed on the problem when a kinetic gelation model with periodically placed initiators [16] was simulated: this showed an amplitude ratio compatible with that of percolation. A likely reason for the observed behaviour is therefore the randomness in the distances separating the initiators in the usual model. This had already been pointed out in [8] but no detailed mechanism was suggested to connect the two effects. Unfortunately, we cannot improve upon this, except to the extent of saying that the effect is almost certainly not a genuine difference, but rather a very prolonged crossover. It would be of considerable interest, in this respect, to see whether a simulation counting the mass in terms of initiators would find an anomalous amplitude

ratio. The reason for this is that, as already noted in the case of the oscillations in the cluster size distribution, the difference between the two ways of counting the mass can still lead to very long-lived, although non-asymptotic, effects.

In the case of the backbone the situation is more complex yet: in this case, even without assuming the lattice independence of d_{BB}, a rigorous result due to van den Berg and Kesten [17] allows us to show an inconsistency between the observed values of β and ν on the one hand and the observed value of d_{BB} on the other. The result can be cast in the following form:

$$d_{BB} \leqslant d - 2\beta/\nu = 2d_f - d. \tag{4.2}$$

As β and ν have been found to be compatible with the percolation values, this yields $d_{BB} \leqslant 2$, in marked contrast to the observed value [7] of d_{BB} of 2.3. The resolution of this discrepancy is somewhat complex and shall be the main object of the following.

First, let us sketch the derivation of (4.2) from the actual result of van den Berg and Kesten. In [18], Chayes and Chayes prove the following fact from the original result of van den Berg and Kesten: if P_∞ is the probability for a site to belong to the infinite cluster and Q_∞ is the probabability of belonging to the backbone, i.e. of being connected to infinity by two disjoint paths, then one has

$$Q_\infty \leqslant P_\infty^2 \tag{4.3}$$

from which (4.2) readily follows under suitable assumptions concerning the uniqueness of the infinite cluster, a hypothesis generally accepted for $d \leqslant 6$. Indeed, the number of sites in the infinite cluster (in the backbone) inside a box of size L is $P_\infty L^d$ ($Q_\infty L^d$). The above result holds for random percolation on an arbitrary translation-invariant lattice, and therefore also for the mole's labyrinth. However, in this case, the quantity Q_∞ does not have the same meaning in the two interpretations. In the case of percolation on the Γ lattice, it indicates the probability that an initiator be connected to infinity by two paths *passing through a disjoint set of initiators.* In the mole's labyrinth, however, in order for a site to belong to the backbone, it is sufficient that it be connected to infinity by two disjoint paths using all the points available. The difference becomes clearest according to figure 1: there the initiator denoted by X clearly belongs to the complement of the backbone in the 'skeletal' view shown in figure 1(a)) that only considers the initiators and the bonds connecting them. However, it belongs to the backbone in the 'full' diagram shown in figure 1(b), since there are two disjoint paths connecting it to infinity. This can be given a formal analogue in the Γ lattice as follows: if the random walks connecting two initiators are such that the two can be connected by two disjoint paths, we connect the corresponding points on the Γ lattice by a double bond. This makes the two definitions of the backbone identical. However, under these circumstances, the derivation of (4.2) is no longer valid in general. Indeed, in a lattice that had only double bonds, one would have $d_{BB} = d_f$, in manifest contradiction to (4.2).

We therefore need to show that the two definitions of the backbone scale in the same way. Let us call the backbone on the lattice with double bonds the extended backbone. This consists of the ordinary backbone together with that part of the dangling ends connected to it by a path consisting entirely of double bonds. If one considers the infinite cluster discarding all single bonds, however, the cluster is separated into a large number of clusters of possibly large but finite size. This is a consequence of the fact that there is a finite probability that a bond is single, so that discarding them all brings one below the percolation threshold. Thus, that part of the dangling ends

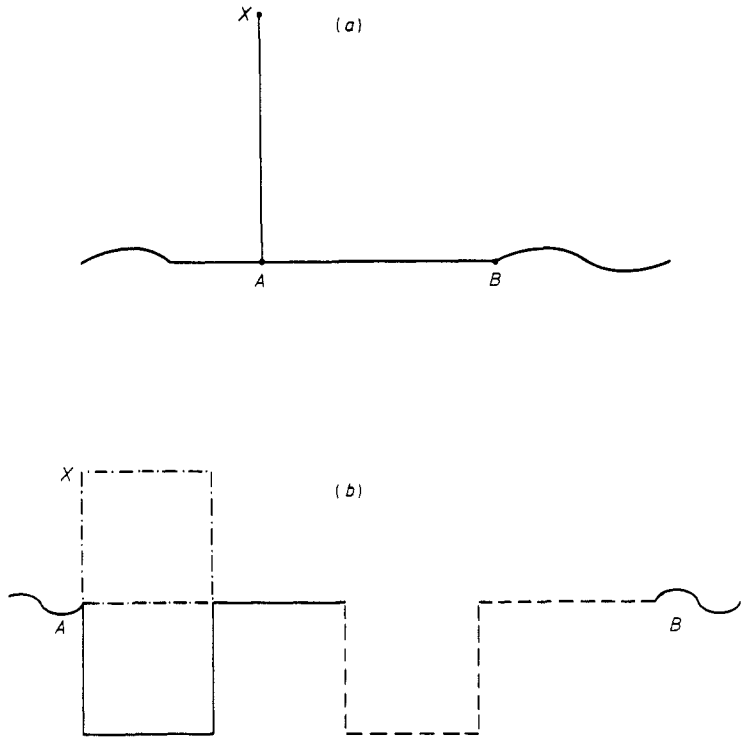

Figure 1. (*a*) and (*b*) show the skeletal and full view of a certain part of an infinite cluster of kinetic gelation. Shown are three initiators, *A*, *B* and *X*. *A* and *B* are both supposed to be connected to infinity, each by its own path (indicated by a wavy line in both figures. Clearly, in (*a*), *X* is a dangling end, whereas in (*b*) it belongs to the backbone. In the latter, the trails of the initiator *A* is shown as a full line, that of *B* as a broken line and that of *X* as chain.

which is tacked on to the ordinary backbone to form the extended backbone consists of clusters of a finite size λ. This means that, to every point of the ordinary backbone, we are adding a finite number of clusters of finite size λ, and therefore the mass of the two backbones can at most differ by a factor λ^d. They therefore scale the same way in the asymptotic limit. This issue brings out the probable reason for the discrepancy between theory and numerical experiment quite clearly, however. In order for the asymptotic regime to be reached, the correlation length ξ must be distinctly large than λ, which may be quite a stringent requirement if the probability for double connection between initiators is high. Again, this might be checked by looking into a ballistic variation of the mole's labyrinth, as pointed out above.

As a final remark on the backbone, let us note that the above model is remarkably consistent with two otherwise quite puzzling facts: these are the values of the exponent describing the scaling of the length of the shortest path as a function of distance and of the diffusion exponent. As noted in the introduction, both of these are compatible with their percolation values. This would not be expected in the case of a fundamental change in the structure of the backbone. This is particularly true of the diffusion exponent, since it determines, via the Einstein relation, the scaling of the two-point conductivity as a function of distance. If, however, the backbone of kinetic gelation effectively consists of segments of dangling ends tacked on to the backbone of a

percolation cluster, these results would be easily understood: no shortest path passes through this additional mass and the current flowing through it is negligible. A test of this hypothesis would be to compute the backbone using only the connections between initiators and measure its fractal dimension. Should it fall close to the percolation value, this would be a distinct argument in its favour.

5. Conclusions

Summarising, we have shown an equivalence between the mole's labyrinth and percolation on a rather complicated lattice. This settles the point of the universality class of the mole's labyrinth model of kinetic gelation at finite initiator concentration: it is the same as percolation and the equivalence to random percolation is exact. Since the peculiarities of the other models of kinetic gelation have all been encountered numerically in the mole's laybrinth, it is reasonable to assume that all these models are in the same universality class as percolation as well, and that the numerical evidence is tainted by crossover effects. Furthermore, as we have shown, these models can all be mapped onto models of percolation with rather complex short-range many-body correlations. This means that for small enough initiator concentration, the correlation length due to these correlations is small and should have no effect on the critical behaviour or on the universality class. While this latter line of reasoning is certainly less convincing than displaying an exact equivalence between two models, it should be sufficient to make suspect any claim of a new universality class in models of the type of kinetic gelation.

To make the equivalence between kinetic gelation and percolation, however, one needs to reckon the mass of a cluster as the number of initiators that were involved in its formation. Although we show that this does not make any difference in the asymptotic limit, very long-lived effects can indeed follow. The oscillations in the cluster size distribution are a case in point. We further show that various other differences are attributable to crossover effects. A conjecture concerning the precise nature of the effect involved in causing the crossover was made for the case of the above-mentioned oscillations as well as for the fractal dimension of the backbone of the infinite cluster. The most important unresolved issue remains the reason for the difference in the value of the amplitude ratio of the susceptibility.

Finally, the following point should be made: at low initiator concentration, many mechanisms combine to make the critical region quite small. This may very well mean that, in actual physical situations, the predictions of percolation are essentially irrelevant and the features typical of kinetic gelation determine the physics.

Note added in proof. After this article was submitted for publication, Dr A González informed me of related work by de Gennes [19] where the mole's labyrinth was first defined (and named 'chain percolation'). His results are parallel to those published here. In particular, he shows that for $d \geqslant 4$, a long mean-field crossover is to be expected if $C_1 \to 0$.

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