ADDITION POLYMERIZATION AND RELATED MODELS

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We present a review of growth models involving the successive union of linear objects in the form of "walks." Two different types of models exist: those having one walk and those with many walks. We concentrate on the polymerization transitions which occur in the second case.

This presentation is dedicated to one of the experimentally and theoretically important growth models namely those in which linear objects i.e. walks are grown. The "growth sites" [1] of these models are simply sitting on one (or both) ends of the walk and their number cannot increase because branching is not allowed. Thus in these models the set of all growth sites is not a (fractal) structure of interest as it is in other models (DLA, epidemics, etc. [2]). The growth sites wander through space (usually a regular lattice) according to a given rule, the "growth rule," leaving behind as their trace the growing walk. Sometimes it is useful to imagine the growth site to be a small animal like an ant that moving around leaves behind on very soft soil a fine trace of footprints.

In order to give a feeling for such a growth mechanism I will present the experimentally important example of "radical initiated addition (co-)polymerization": The starting configuration consists of non-polymerized "monomers" that are molecules which have double bonds. Let us first consider the case where a monomer has only one double bond as for example the monoacrylamide shown in Fig. 1a. To initiate the growth reaction one adds an "initiator," like ammonium persulfate. The initiator dissociates into two radicals when then try to saturate their unbound electron. To do so they open up the double bond of one monomer. But now the other carbon atom of the opened double bond is unsaturated and it will look for the double bond of another monomer which it will open up. In this way two monomers will be connected to each other. Furthermore, there will still be an unsaturated electron at one end which will now make the connection to the next monomer and so forth. The way the reaction proceeds the polymer chain grows longer and longer and the only really moving part is the unbounded electron which corresponds to the growing site (ant) of this model. The resulting walk (Fig. 2a) cannot crosslink and is thus technically speaking a self-repelling walk (kinetic growth walk (KGW) [3]).

\[ HC = \text{CH}_2 \]
\[ R \text{H} \]
\[ (a) \]

\[ HC = \text{CH}_2 \]
\[ R \]
\[ H_2\text{C} - \text{R} - \text{H} \]
\[ (b) \]
\[ \text{CH}_2 \]

FIGURE 1
(a) Monoacrylamide (b), bisacrylamide, the test-R has the form O=C-NH.

FIGURE 2
(a) Walk that cannot crosslink (b) walk which is two-tolerant in some points. Dots are two-functional sites and circles are four-functional sites.

If some of the monomers now have more than one double bond (for example two double bonds as in the case of the bisacrylamide of Fig. 1b) then the chain can intersect itself in these monomers; in the case of the bisacrylamide it can intersect once (Fig. 2b). The maximum number of bonds a monomer can have is called its "functionality." In Fig. 2 the dots are two-functional sites and
the circles four-functional sites. In the circles of Fig. 2b the walk is called "two-tolerant" because the walk tolerates up to two times crossing a circled monomer. If $C_2$ is the concentration of two-functional monomers and $C_4$, the concentration of four-functional monomers the concentration of two-tolerant points on the walk is $C_4/(C_2+C_4)$.

If the monomers and the polymer chain can move completely freely it will always be possible to feed the unsaturated electron with more monomers and the chain may grow forever. This picture of "infinite mobility" can be described well by reaction equations (mean field); but it is not very realistic because for finite tolerance there are "steric hindrance" effects and knots in the chain (entanglements). Steric hindrance means that the growth site cannot cross a certain region of space simply because there are parts of the chain or of other chains in its way which the walk can neither crosslink nor go around. In two dimensions this effect is especially strong because of the high return probability and the fact that a linear object can serve as a frontier in a plane. In higher dimensions it is essentially the finite volume that a real chain occupies which produces the hindrance. The strongest effect of steric hindrance is termed 'trapping', i.e. when a growth site gets into a cage from which it can never escape again. These effects of steric hindrance even in the form of trapping are also found in experiments.

In most of the theoretical models that we will study here we assume the monomers to have zero mobility and to sit on the sites of a regular lattice. In this case the effects of steric hindrance are usually stronger than those found in experiment. One possibility to get around steric hindrance effects completely is to consider the case of infinite tolerance, i.e. to take random walks, and that is often done to simplify the situation.

As usual for growth models there is a big variety of growth rules that one can invent for the movement of the growth site (ant) and each rule represents a different growth model. Let me list some examples only for one-tolerant walks: 1) the self-avoiding walk (SAW) which corresponds to a "blind" (no knowledge about the surrounding) and "drunken" (random choice of the direction) ant which has only one chance, i.e. it stops forever whenever it has tried to hit its own trace. 2) the kinetic growth walk (KAW) [3] which corresponds to a blind and drunken ant that has unlimited number of chances (but also cannot cross its trace). 3) the "myopic" and drunken ant which has knowledge about its trace in a near surrounding and uses this knowledge to try to avoid trapping [4]. (Nevertheless it will be trapped in two dimensions after some time with probability one.) 4) the "intelligent" and drunken ant which has knowledge about its whole trace and which by never passing through certain gates will never get trapped [5]. 5) the "half-drunk" ant (blind, myopic, intelligent) which with a certain rate prefers to go straight, i.e. in the same direction it went in its previous step. 6) ants (drunken, half-drunk, blind, myopic, intelligent) that have some longer range attraction or repulsion to their own trace. Similar definitions could be put forward for k-tolerant walks. One additional rule that is of interest for k-tolerant walks is to have these walks to be "n-folding" ($n<2k$). This means that the walk can only go up to n times over the same "bond", i.e. connection between two nearest neighbor sites.

Many more rules are possible but only very few have actually been studied. The impression that one gets from the cases that have been studied is that the rules for the ant are "relevant" properties of the walk in the sense that they change its "fractal dimension." On the other hand properties of the sites of the lattice like the tolerance, the distribution of the tolerances, the lattice symmetry or the mobility of unpolymerized monomer seem not to be relevant. The situation is similar to that of diffusion limited aggregation (DLA)[6] where properties of the diffusion field (random, ballistic, directed, dolphin) seem to be relevant while the attaching rules (sticking probability, short-range attraction, next nearest neighbor connection, etc.) seem to be irrelevant:

<table>
<thead>
<tr>
<th>walks</th>
<th>DLA</th>
</tr>
</thead>
<tbody>
<tr>
<td>relevant</td>
<td>rule for ant</td>
</tr>
<tr>
<td>irrelevant</td>
<td>monomers</td>
</tr>
</tbody>
</table>

The growth models presented here are purely geometrical models, no thermal equilibrium is involved and all information is contained in the geometrical structure in space. For geometrical models there are usually two "critical phenomena" that one can study:

1. The first are the "scaling" properties of one walk. In this case the critical point is located in the limit $1/N=0$ where $N$ is the number of "units" of the walk. A unit is the piece of walk constructed at one growth step. The scaling properties are described by the fractal dimension (in the general case of geometrical models also by the spectral dimension, topological dimension, backbone fractal dimension, etc.[2]).

The other critical phenomena, which we want to study in the rest of this presentation, is given if one considers many walks growing simultaneously. In some points at least distances must be able to crosslink, i.e. some of the sites have to be at least four-functional. In the initial stage when no walk has yet touched another walk each walk is a "cluster" of size N. (The number of units N varies from walk to walk for most growth rules.) When during the growth
one walk (N1 units) crosses another walk (N2 units) these two walks become one sole cluster of size N1+N2. The growth rule is not altered by the merge of two clusters to a bigger one. Only the "cluster size distribution" n0 namely the number of clusters of size s (per volume) does change with "time." Time can be defined as the attempts to grow a walk or the successful attempts to grow a walk both divided by the number of walks. The critical point in these models will be the critical time or "gelpoint" tC at which n2, or more precisely the moments of n2, become singular. The singularity at tC comes about because at this time for the first time an infinite cluster appears. This "incipient infinite cluster" is generally "spanning," i.e. connecting from one side of the recipient to the other.

The language introduced above strongly reminds us of percolation where tC corresponds to the percolation threshold but the kinetic aspect of our models makes them, as we will see, fundamentally different from percolation. In experiment the critical point corresponds to the "sol-gel transition" [7]: Before reaching the sol-gel transition one has a viscous soup of small polymers, the sol, and after the transition there is a spanning network through this soup; the gel, which gives a macroscopic elasticity to the whole system. This experimental realization of many-walk growth models has given them the generic name of "kinetic gelation."

The easiest model of this kind that one can imagine is the "mole's labyrinth" [8] where all the sites have infinite functionality and the ants are blind and drunken, in other words, the walks are random walks. One knows that random walks are two dimensional objects and probability that two walks will ever cross each other's trace is strictly smaller than one. Thus for d=2 two neighboring walks are "quasi-transparent" to each other, and so a given walk can crosslink with finite probability another walk arbitrarily far away before having crossed any other walk. This was just the condition for mean field to be valid (infinite mobility condition) because in this case the specific local geometrical configuration around a given walk becomes unimportant and the other walks appear only as a mean regardless of their distance to the given walk (Flory-Stockmayer theory). The fact that mean field becomes valid for d>4 implies that the "upper critical dimension" d_u of this model is d_u=4.

This is clearly different from percolation for which d_u=6 and is evidence that the models belong to different "universality classes." Up to now among the grown walk Listed previously all those that have been studied in detail have turned out to be two dimensional, walks for d=4. This is true for the k-tolerant SAW, the KGW and even the "true self avoid walking" (TSAW)[9]. So I conjecture that in all cases the upper critical dimension for kinetic gelation might be d_u=4.

A very important parameter in the kinetic gelation models is the "concentration of initiators" C_i which corresponds to the number of walks that one has started to grow per volume. C_i can be fixed at the beginning or (constant) increased as time goes on. C_i is also an upper bound for n2. The distribution of initiators, i.e. of sites where walks start to grow, can be done regularly or at random. The concentration of growth sites equals C_i unless one specifies mechanisms in the model which can destroy growth sites as "annihilation" or "poison." Annihilation means that when two growth sites are simultaneously on the same lattice site they are both annihilated. Poison means that one specifies certain lattice sites that swallow growth sites. Both effects are of experimental interest.

Most information that we know about kinetic gelation models comes from numerical simulations. The study of the whole cluster size distribution function n2 can be very interesting and surprising (see eg. [10]) but requires also very much numerical effort. So it is convenient to study for instance only the second moment

\[ x = \langle N_2 \rangle = \frac{\langle N_2 \rangle^2}{\langle N \rangle^2} \]

s_w being the size of the largest cluster and \( L \) the size of the box in which the simulation takes place. Near the gelpoint one expects a relation \( x = C_4(t-t_c)^{-\gamma} \) for \( t\to t_c \) and 

\[ x = C_4^2(t-t_c)^{-2\gamma} \]

for \( t=t_c \) to be valid and can hope that as for percolation that \( \gamma \) and \( R = C_4^2/C_\gamma \) are universal numbers. \( \gamma \) and \( R \) are obtained from simulations from direct log-log plots and also using finite size scaling [8,11].

The realistic kinetic gelation model that has been most thoroughly studied and that historically started the whole field this presentation is about is a model tailored specifically to explain the experimental situation. It was proposed by M. Adam in Saclay, presented at a conference by Manneville and de Seze [12], and for the first time studied in detail in Ref. 11. It has two and four functional sites and in some cases [13,14] "solvent" (zero functional) sites with a concentration \( C_4 = 1-C_2-C_4 \). Initiators are distributed randomly and only at the beginning of the reaction. Growth sites are blind and drunken and do annihilate each other. There are no folding restrictions and there is no poison.
In three dimensions this model yields for $C_5 = 0$ [11]:

<table>
<thead>
<tr>
<th>$\gamma$</th>
<th>R</th>
<th>$C_1$</th>
<th>$C_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0±0.2</td>
<td>2.7±0.8</td>
<td>0.003</td>
<td>1.0</td>
</tr>
<tr>
<td>2.0±0.2</td>
<td>3.2±0.9</td>
<td>0.003</td>
<td>0.1</td>
</tr>
<tr>
<td>2.3±0.4</td>
<td>1.7±0.6</td>
<td>0.0003</td>
<td>1.0</td>
</tr>
<tr>
<td>1.8±0.3</td>
<td>4.2±1.2</td>
<td>0.03</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 1

The corresponding values for percolation are $\gamma = 1.9±0.1$ and $R = 10±3$. Table 1 shows the striking feature that $R$ depends strongly on $C_1$, the stronger the more $C_1 > 0$. The dependence can be really continuous or more likely due to a cross-over phenomenon but the question remains yet open. Also $\gamma$ seems to systematically depend on $C_1$ but the error bars are too large to make a definite statement. For comparison let us look at the results for the moles labyrinth in $d=3$ [8]:

<table>
<thead>
<tr>
<th>$\gamma$</th>
<th>R</th>
<th>$C_1$</th>
<th>initial distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4±0.4</td>
<td>7±2</td>
<td>0.001</td>
<td>regular</td>
</tr>
<tr>
<td>3.4±0.6</td>
<td>6±3</td>
<td>0.000125</td>
<td>regular</td>
</tr>
<tr>
<td>2.6±0.5</td>
<td>2±1</td>
<td>0.001</td>
<td>random</td>
</tr>
</tbody>
</table>

Table 2

Here we see the same trend as in Table 1 in the changes of $\gamma$ and $R$ if one varies $C_1$, but only the change in $\gamma$ noticeably touches the error bars. Other features that one obtains from Tables 1 and 2 are that also the initial distribution of initiators seems to be relevant while the functionality of the sites (even for the solvent [13]) is irrelevant.

In two dimensions the situation seems to be numerically much more difficult: on one hand because of the stronger trapping effects, and on the other hand there might also be logarithmic prefactors present (because also in the case of the mole's labyrinth there is very much curvature in the raw data [8]). The mole's labyrinth yields values for $\gamma$ and $R$ compatible with percolation. The realistic kinetic gelation model has been treated in many publications and by many authors, in most cases not very successfully. Even some static large cell renormalizations [15] and calculations of fractal dimension of the largest cluster [16] have been performed. The most accurate data suggest that the fractal dimension is the same as percolation and does not change with $C_1$.

Another interesting variation of the mole's labyrinth model which shows a sensitive effect on the growth sites is the model of ants with hard core repulsion. Experimentally this might to some extent model ionic initiated reactions where the growth sites have strong electrostatic repulsion. One starts with a regular initial distribution of the ants so that their initial distance is $b = C_1^{-\alpha}$. During the growth one insists that two ants can never come closer to each other than $\alpha \cdot b$ ($\alpha \leq 1$). For $\alpha = 1$ all the ants would have to make synchronous movements like soldiers in order to maintain their mutual distance fixed. Thus in the case $\alpha = 1$ one expects to find a first order transition because the mean cluster size will discontinuously jump from a finite value to infinity. For $\alpha = 0.8$ we see in Fig. 3 a log-log plot of $x$ against $|p-p_c|$ in $d=3$. Clearly in this case $R < 1$ which has not been found in any of the previous cases. The value of $\gamma$ could be smaller above $p_c$ than below but as the finite size effects are so strong no definite conclusion can be drawn.

![Figure 3](image-url)

**FIGURE 3**

Log-log plot of $x$ against $|p-p_c|$ for $\alpha = 0.8$, $C_5 = 0.001$, system size $L = 30$ in $d = 3$; crosses for $p > p_c$, dots for $p < p_c$.

Summing up the results for kinetic gelation models we conclude that in $d = 2$ it is difficult to obtain results and so no evidence has been found that the behavior is different from percolation. In $d = 3$ the critical quantities $\gamma$ and $R$ seem to be those related to the growth sites (concentration and initial distribution of initiators, repulsion, perhaps also the creation of new initiators in time [17]). Irrelevant parameters are those related to the monomers (tolerance, existence of solvent, lattice structure and the mobility of monomers). So the partition between relevant and irrelevant effects is similar as those of the one-walk problems. In $d = 4$ we expect the Smoluchowski equations to be valid (see presentations by Benedek, Ziff and Levy in these proceedings) because $d = 4$ is the upper critical dimension.
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(4) N. Jan, private communication.
(5) See J.W. Lyklema and K. Kremer in these proceedings.
(10) A. Chhabra, D. Matthews-Morgan, D.P. Landau and H.J. Herrmann, preprint and these proceedings.
(17) See D. Matthews-Morgan and D.P. Landau in these proceedings and to be published.