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Crossover from gelation to precipitation

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Abstract. — Gelation and precipitation are two possible outcomes for the polymerization of monomers dissolved in a solvent. Gelation is obtained when the polymers grow with a fractal dimension $d_f$ lower than 3; precipitation when $d_f$ equals 3, i.e. when they are dense. In sol-gel processes, a continuous range of final products may be obtained, with fractal dimensions ranging from $d_f < 2$ (gelation of branched polymers) to $d_f = 3$ (precipitation of dense particles). We show that the selection of the growth process (and of the final state) may result from the relative reactivities of monomers with different chemical environments. If reacted monomers are much less reactive for further reactions, the system starts with pairs and then oligomers; the recombination of polymers through the tips of branches leads to gelation. If monomers are much more reactive when they have already made some bonds, then the densest clusters scavenge everything else in the reaction bath: this is precipitation. Systems used in actual sol-gel processes have a weaker hierarchy of chemical reactivities; then the reaction bath may cross over during reaction from recombination of bushy polymers to precipitation of the densest one. This allows control of gel structure through manipulation of chemical preferences.

1. Introduction.

Inorganic gels may be produced through the polymerization of organometallic precursors dissolved in a weakly polar solvent [1-3]. In such « sol-gel » processes, bushy structures are formed through the continuous recombination of branched polymers [4-6]. When the connected structures reach a macroscopic size the reaction bath becomes a gel; the solvent, byproducts of the reaction and unreacted species are trapped within the macroscopic network.

However a gel is not the only possible outcome for such polymerization reactions. Other final states may be reached, including sols where the polymerized structures did not reach macroscopic sizes, and precipitates where the reactions produce dense structures rather than tenuous ones [7]. The gels may also differ according to the conditions of the reaction, some being more lumpy or with a larger mesh size than others. It is now established that the choice of final state is made through the addition of solvent and of chemical modifiers.
The solvent plays an essential role in sol-gel processes because it allows different types of structures to grow from the same mixture of components. At the beginning, the dilution imposes a reaction mechanism through diffusion and collision; this resembles particle aggregation mechanisms in solution rather than the percolation mechanism which applies in concentrated systems. Then, when the polymers grow, they are swollen by the solvent; this determines the relative locations which neighboring polymers may occupy within the reaction bath. Similarly, the final gel is still swollen by the solvent, and this swelling determines its mechanical properties; in this sense the gel is a one-phase system, whereas the precipitate is a two-phase system.

Even more important are the chemical modifiers which are added to the solvent in order to select certain types of reactions [8]. They include organic complexants (ligands) which bind to the monomers, and electron donors or acceptors which modify the partial charge of reactive groups [9]. A particularly impressive example of chemical selection is the growth of TiO₂ gels from Ti(OBU)₄ with modification through H⁺ ions [10]. In this case, a continuous range of final products may be obtained, including sols, gels and precipitates, according to the concentration of H⁺.

Even though chemical modification has been immensely successful, there is no systematic interpretation of how it allows specific structures to be selected. Current models for aggregation in solution are based on random diffusion, reaction and collision of clusters; they produce universal growth patterns, where tenuous polymers recombine to form similar tenuous polymers; the fractal exponent which describes this selfsimilarity is always $d_r = 2$ [11]. Growth of dense clusters is predicted when it is assumed that the reactions are only between small clusters and larger ones, as in the Eden model; however there is nothing in the model that justifies this assumption [11]. In general, models which include geometrical features only are not expected to reproduce a pattern of chemical selection between different types of growth.

In this paper we present a model which describes the selection of growth patterns according to differences in chemical reactivity. The critical feature is that reactive monomers in a dense region of a cluster do not have the same reactivity as other monomers on branches or tips. Chemical modification changes the difference in reactivity between them; accordingly, dense regions grow faster than tips or vice versa. This model produces universal behavior in the classical limits, i.e. linear growth when the tips grow much faster, recombination of branched polymers when all reactivities are equal, and dense growth when highly coordinated monomers are the most reactive. In addition, it also produces a continuous range of non universal growth patterns between these limits.

2. A simplified view of sol-gel reactions.

Sol-gel processes start with a precursor, which usually is a metal alkoxide M(OR)₅. This precursor is hydrolyzed into reactive monomers according to a set of successive reactions:

$$\text{M-OR} + \text{HOH} \leftrightarrow \text{M-OH} + \text{ROH}.$$  (1)

Then hydrolyzed groups can react with each other or with unhydrolyzed groups through condensation reactions:

$$\text{M-OH} + \text{R-OM} \leftrightarrow \text{M-O-M} + \text{ROH}$$  (2)
$$\text{M-OH} + \text{H-OM} \leftrightarrow \text{M-O-M} + \text{HOH}.$$  (3)

These condensation reactions are largely irreversible under usual reaction conditions, because oxo bridges are quite strong. Hence they trap the system into a set of permanent bonds. Extensive condensation leads to the formation of the oxo-polymers which build the gel network.
In general, the set of hydrolysis and condensation reactions which operate in a given reaction bath can be extremely complex: indeed hydrolysis reactions may produce 4 different monomers, which may react with each other or with the precursors; then the condensation products may get hydrolyzed further or condense with other species; thus even for oligomers the number of reaction paths is huge. However there are two comparatively simple situations: (a) that where hydrolysis is incomplete and rate limiting, whereas condensation is fast; (b) that where hydrolysis is fast and complete, whereas condensation is slow and incomplete.

In order to be successful, chemical modification must act on the set of reactions which is rate limiting. Consider for instance the situation where condensation is limiting: then the aim of chemical control (modification) would be, in some cases, to prevent further condensation of partially condensed regions of a polymer, and in other cases to promote such condensation. This will be achieved if the probability of further condensation for each monomer depends on the number of bridges already made, and if this dependence can be manipulated through the addition of chemical modifiers.

A similar analysis holds for chemical control in the situation where hydrolysis is the rate limiting step. In this case, every hydrolysis of an M-OR group is immediately followed by a condensation on the resulting M-OH function according to reaction (2). Here chemical control must act on the probability of a further hydrolysis on the same metal: if it is inhibited by a previous hydrolysis of other groups, then dense regions will be prevented from getting denser, and growth will occur mostly at the tips of branches. On the contrary, if previous hydrolysis of adjacent groups makes a M-OR function more reactive, then dense regions will be the main growth centers, and the denser they are the more they will scavenge everything else in the reaction bath.

Thus in both situations the key to chemical control of growth patterns is the difference in reactivity between monomers which already have been reacted 0, 1, 2 or 3 times. There are many examples where these reactivities are indeed different, and where their hierarchy can be changed through chemical modification. For instance, in Ti alkoxide condensation at low hydrolysis ratios, the more hydrolyzed Ti are also the more susceptible to further hydrolysis; however the order is reversed by protonation of the -OR groups [12]. Accordingly, we would expect unprotonated solvents to favor the growth of dense regions where the Ti which are already hydrolyzed and bridged become more reactive; to the contrary, we can expect protonated solvents to favor the growth of linear structures. This analysis is supported by observations: precipitates are obtained at low H+/Ti ratios, and gels at high H+/Ti ratios [13].

3. Numerical model for chemical selection and binding.

In this section we construct an aggregation model which incorporates the pattern of chemical selection described above. This model is based on earlier ideas from Leyvraz [14] and from Meakin [15]. First we define a mathematical function which describes the differences in reactivity between monomers with various numbers of bridges. Then this function is used to generate statistical weights for all monomers in a collection of polymers. Finally the polymers are reacted according to these statistical weights, and configurations where they overlap are rejected. After a successful reaction the statistical weights are changed to take into account the new bridges, and the new collection of polymers is taken up for further reactions.

Differences in reactivity are described as follows. The monomers are labeled with indices 1 ... i ... n. At any cycle of the simulation, a count is taken of the number \( v_i \) of bonds established by monomer \( i \) (and by every other one) (this number is a local connectivity). Now we must build a function \( f(v_i) \) which expresses how the reactivity of monomer \( i \) varies with
v_i. We know that in some systems the tips of branches will be the most reactive sites, hence \( f(v_i) \) will be a decreasing function of \( v_i \); in other systems the dense clusters will be more reactive, hence \( f(v_i) \) will be an increasing function of \( v_i \). A natural choice for the function \( f \) is an exponential with \( v_i \) in the exponent; indeed the reactivity is governed by thermal activation into a transition state, and we assume that the activation energy depends on \( v_i \). We choose:

\[
f(v_i) = w^{v_i}\tag{4}
\]

where \( w \) is a parameter which describes the pattern of chemical selection. Values of \( w \) which are smaller than 1 yield a reactivity which decreases with the number \( v_i \) of bonds already formed; for \( w = 0.1 \) isolated monomers will have the highest reactivity \( (f(0) = 1) \) and form pairs readily, chain ends will be next \( (f(1) = 0.1) \), and chain branching should be relatively rare \( (f(2) = 0.01) \). Values of \( w \) which are larger than 1 yield a reactivity which increases with \( v_i \): for \( w = 5 \) the reactivity of monomers with already 3 or 4 bonds is so high that, as soon as they appear, they will become the only growth sites.

Now we are in a position to select some monomers, free or already bound to polymers, for a coming reaction. This selection is done according to the statistical weights defined by the reactivities of each monomer: if \( f(v_i) \) is the reactivity of monomer \( i \) having \( v_i \) bonds already reacted, then the probability of selecting \( i \) will be:

\[
\omega_i = \frac{f(v_i)}{\sum f(v_i)}.
\tag{5}
\]

At every cycle of the simulation we choose 2 monomers \( i \) and \( j \) at random, according to the collection of statistical weights. These monomers may be free or they may belong to previously made polymers. If they belong to the same polymer they are rejected. We then try to react \( i \) and \( j \) together by bringing them into neighboring positions. This is done according to spatial rules which are defined next.

The spatial rules determine the relative positions of polymers during a reaction. The first rule places the monomers on the sites of a lattice. The functionality \( z \) of the lattice is chosen to match that of the monomers; in our case the lattice is simple cubic with \( z = 6 \). This rule is convenient for recognizing which monomers are bound: any two monomers which occupy adjacent lattice sites are assumed to be bound to each other. It is well suited to describe highly reactive species, such as monomers used in sol-gel processes; however it makes it impossible to also describe the polymerization of chains with excluded volume.

The second rule forbids the use of a lattice site by more than one monomer; hence neighboring polymers may not overlap. This is the rule which causes fractal growth in cluster-cluster aggregation models: indeed bushy clusters of similar sizes cannot interpenetrate, hence voids as large as the cluster size are created when 2 clusters bind. Because of this rule the true reaction probabilities of monomers differ from their reactivities (statistical weights in the selection process): monomers near the center of a polymer are hardly accessible at all, hence their reaction probability is low even if their reactivity is high; thus densification at a late stage of growth is difficult. On the other hand, monomers near the periphery will react more frequently, with probabilities close to their statistical weights.

With these ingredients the model attempts to produce a successful collision between monomers \( i \) and \( j \). A configuration is chosen at random, where \( i \) and \( j \) occupy neighboring lattice sites, and the relative positions of the polymers to which they belong are examined. If they overlap, the configuration is rejected, and a new pair of monomers is selected; this simulates the fact that the polymers will bounce off each other if the collision is unsuccessful. If they do not overlap, then the 2 polymers are bound through \( i \) and \( j \), and the collection of
polymers is modified accordingly. Then the reaction « time » is incremented by one unit, and the process is iterated. The process ends when all monomers are bound in a single polymer. Thus the reaction « time » may be defined as \( t = (n - m)/n \) where \( n \) is the number of monomers and \( m \) the number of independent objects in the collection. This time is not simply related to real time; rather it measures the progress of the reaction.

4. Results.

The central question is, of course, whether the model can reproduce a continuous crossover between gelation and precipitation. For this reason, we first present results concerning the structure of the final polymer. The requested outputs are: (a) whether or not it is a dense object; (b) if it is not dense, whether it is selfsimilar; (c) if it is selfsimilar, what is its fractal dimension. We find that the answers to these questions depend on the parameter \( w \) which describes the pattern of chemical selection. Then we analyze the types of growth which lead to the different final states.

**Final state.** — Pictures of the final polymers obtained through the binding of 1 024 monomers at various values of \( w \) are presented in figure 1. The monomers are shown as small spheres, and the polymer as a 3-dimensional aggregate projected onto the plane of the figure, with a slight shift and a darker shade for monomers located further back from the front of the aggregate. Because of the projection the polymers appear denser than they really are; indeed the polymer obtained at \( w = 0.2 \) is largely linear, and that made at \( w = 1 \) is expected to have a fractal dimension close to 2. The polymer grown at \( w = 3 \) is a crystal shaped as an octahedron; the crystalline structure is imposed by the lattice, and the shape is favored because it minimizes its surface area.

The spatial organization of each polymer may be assessed from the pair correlation function of all monomers, or from its Fourier transform which is the scattering function of the polymer. This is calculated as a sum over all distances \( r_{ij} \) separating pairs of monomers:

\[
I(Q) = \sum_i \sum_j \frac{\sin Q \cdot r_{ij}}{Q \cdot r_{ij}}
\]  

Accordingly, the scattered intensity starts at \( Q = 0 \) from a value proportional to the square of the number of monomers, and decays with increasing \( Q \) at a rate determined by the number of pairs with separation \( Q^{-\ell} \). For statistical aggregates, 3 parameters may be extracted from this decay: (a) At low \( Q \) values the curvature of the scattering curve yields the overall radius of gyration \( R_g \) of the polymer. (b) At intermediate \( Q \) values the rate of decay is determined by the dimensionality of the structure: linear structures yield a \( Q^{-1} \) decay, platelets \( Q^{-2} \), and dense structures \( Q^{-4} \). Intermediate exponents are obtained with fractal structures: mass fractals with fractal dimension \( d_f \) between 1 and 3 give \( Q^{-d_f} \); surface fractals with surface dimension \( d_s \) between 1 and 3 give \( Q^{(6 - d_s)} \); the limiting behavior \( Q^{-3} \) is obtained with dense objects with an infinitely rough surface. (c) At high \( Q \) the scattering curve shows 2 peaks corresponding to distances between neighboring monomers on the lattice; the height of each peak is related to the number of neighbors at the corresponding lattice distance.

Figure 2 shows the calculated scattering curves for polymers grown at various values of \( w \). It shows the same trend which was obvious in the pictures of figure 1: polymers grown at low values of \( w \) give low slopes in the intermediate range, and polymers grown at high values of \( w \) give higher slopes. However the aggregates are not large enough to give a full power-law behavior: the selfsimilar behavior only extends for one decade in \( Q \) values. Rather than
Fig. 1. — Pictures of polymers constructed from 1 024 monomers at different values of the chemical selection parameter $w$. The scattering curves calculated for these polymers are shown in figure 2, and their fractal dimensions in table I.
Fig. 2. — Scattering curves calculated for polymers constructed at different values of the chemical selection parameter \( w \). The curvature at low \( Q \) describes the overall sizes and shapes of the polymers: tenuous polymers have larger radii, hence the downward curvature is at lower \( Q \); dense polymers have small radii, and the curvature is sharp because it reflects the particle shape oscillations, as in a dense sphere. The slope at higher \( Q \) describes the internal structure of the polymers, and the peak at the high \( Q \) end corresponds to nearest neighbor distances between monomers.

trying to determine an exponent from the slope, it is better to fit the whole scattering curve with the Fisher-Burford approximation [16]:

\[
I(Q)/I(0) = [1 + Q^2 R_g^2 (3d+2)]^{-d/2}
\]

(7)

Table I presents the values of \( R_g \) and \( d_f \) which are obtained from the fits; also shown are the values of the average functionality \( v_{av} \) of a monomer, which are obtained directly from the monomer coordinates stored at the end of the simulation. These values show that the average functionality and fractal dimension increase together and continuously as \( w \) is raised from 0.01 to 5. At \( w = 1.6 \) the exponent \( d_f \) reaches \(-3\), indicating that the polymers are dense objects with an irregular surface, as explained above; beyond this point the exponent continues to vary and approaches the Porod exponent of \(-4\) with is expected for dense objects with a smooth surface. The last curve also shows the shape oscillations which result from the nearly spherical shape of the polymer.

**Kinetic Analysis.** — The kinetic analysis is performed by calculating, at every cycle of the simulation, the number of bridges established by each monomer. From these data, we calculate the average functionality and the total numbers of monomers with 0, 1, 2, \ldots bonds. First consider the evolution of the average functionality, which determines the local structure of the polymers. This is presented in figure 3, as a function of reaction time, i.e. number of successful collisions.

At very low values of \( w \), the average functionality grows linearly with a slope of 2. This reflects the formation of pairs and their recombination into linear oligomers and polymers: at each step the number of objects decreases by 1, and the number of reacted functions increases by 2. The final functionality is 2, since all monomers are collected in a single linear polymer.
Table I. — Radius of gyration $R_g$ (in lattice steps), fractal dimension $d_f$ and average functionality $v_{av}$ of the final polymers grown from 2,048 monomers at various values of the selection parameter $w$. The polymer built at $w = 2$ is dense with a rough surface : (slope of the scattering curve 3.9); the polymer built at $w = 3$ is dense with a smooth surface (slope − 4). 

<table>
<thead>
<tr>
<th>$w$</th>
<th>$R_g$</th>
<th>$d_f$</th>
<th>$v_{av}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>300</td>
<td>1.75</td>
<td>2.57</td>
</tr>
<tr>
<td>0.4</td>
<td>195</td>
<td>1.95</td>
<td>2.74</td>
</tr>
<tr>
<td>0.8</td>
<td>95</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>102</td>
<td>2.35</td>
<td>3.24</td>
</tr>
<tr>
<td>1.4</td>
<td>67</td>
<td>2.7</td>
<td>3.9</td>
</tr>
<tr>
<td>2.0</td>
<td>28.5</td>
<td>3.0</td>
<td>4.92</td>
</tr>
<tr>
<td>5.0</td>
<td>27</td>
<td>3.0</td>
<td></td>
</tr>
</tbody>
</table>

At intermediate values of $w$ the average functionality starts with the same slope, because the initial steps still must be the formation of some pairs; then at a time $t_0$ it crosses over to a steeper rise. Finally at very high values of $w$ the crossover occurs right after the first few pairs have formed; from then on the functionality grows linearly with a slope which is close to the coordination $z$ of the lattice.

A detailed view of the chain branching process may be obtained by examining the individual numbers of sites with 0, 1, , $z$ bonds. These are presented in figure 4 for the case $w = 0.01$. In this case pair formation is the only reaction until $t = 0.5$. At this stage all monomers have been used up, and the pairs recombine to form linear chains and cycles. Chain branching starts about $t = 0.6$, and higher coordinations are avoided almost until the end. At intermediate $w$ (Fig. 5), branched polymers appear at $t = 0.3$, and they dominate throughout the rest of the reaction. At high $w$ (Fig. 6) linear structures and cycles are formed right from the beginning. Higher coordinations appear together near $t = 0.2$; the more reactive ones ($v = 4$ and 5) never get numerous because they are immediately transformed to $v = 6$; hence there is a drive towards fully dense clusters.

It is also instructive to examine how free monomers are consumed (Fig. 7). At low $w$, pair formation uses 2 monomers at each cycle, until the supply of monomers is exhausted; this is continued by the recombination of pairs into linear oligomers, which is indicated by the decay in the number of chain ends (Fig. 4). At high $w$, only one monomer is used at each cycle: these monomers are captured by larger, denser polymers. These behaviors were expected; what is remarkable is the behavior at intermediate $w$, where the bath starts with pair formation, crosses over to the formation of denser polymers which condense together (flat section in the curves, no monomers are used) and then densify by capturing the remaining monomers.

Finally consider how the largest polymer grows. Figure 8 shows the variation of mass vs. size for the largest polymer of the collection. In this representation, the slope of the data
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Fig. 3. — Evolution of the average functionality for polymers grown from 128 monomers. Horizontal axis: reaction time, defined as the number of successful collisions; this is also a measure of the connectivity of the reaction bath. Vertical axis: average functionality for all the monomers, isolated or in polymers.

Fig. 4. — Evolution of the numbers of sites with coordination \( v = 0 \) to 6 bonds. The value of the chemical selection parameter \( w \) has been set to 0.01, indicating a higher reactivity for monomers and chain ends. The polymers are grown from a collection of 128 monomers.

yields an exponent which defines the dimensionality of the polymer; if the growth is selfsimilar, this slope is identical with the fractal dimension determined from the pair correlation function, because the structure repeats itself at larger and larger scales. The first selfsimilar regime is linear growth; this yields a slope of 1.7, close to that determined from the
Fig. 5. — Evolution of the numbers of sites with $\nu = 0$ to 6 bonds. The value of the chemical selection parameter $w$ has been set to 1, indicating equal reactivities for all monomers regardless of their coordination.

Fig. 6. — Evolution of the numbers of sites with coordination $\nu = 0$ to 6 bonds. The value of the chemical selection parameter $w$ has been set to 5, indicating a higher reactivity for highly coordinated monomers.

scattering curve which is 1.75. This regime is followed at time $t_e$ by a regime where branched polymers recombine to form similar branched polymers; in this regime the slope is 2.1. Finally at a time $t_d$ comes a regime where the slope is close to 3; this is the densification which results from the capture of the remaining monomers.
Fig. 7. — Consumption of free monomers for growth modes at low, intermediate and high $w$. Horizontal axis: reaction time; vertical axis: number of remaining free monomers. At $w \ll 1$ pair formation is dominant; it uses 2 free monomers for each successful reaction (slope $-2$). At $w \gg 1$ the dominant regime is the capture of a free monomer by a polymer; it uses only one monomer per cycle (slope $-1$). At intermediate values of $w(\sim 1)$ there is a plateau where fewer free monomers are consumed: this corresponds to the recombination of polymers which leave aside the less reactive monomers.

Fig. 8. — Growth of the largest polymer in the collection. Horizontal axis: radius of gyration of the polymer, in lattice spacings. Vertical axis: mass of the polymer, expressed as a number of monomers. Log scales are used for both axes; in this representation a selfsimilar growth process should follow a straight line. The crossovers indicated by arrows correspond to the onset of branching; the positions of the arrows correspond to reaction times calculated in Appendix A.
5. Discussion.

The model generates two sets of data which pertain to the chemistry and to the physics of sol-gel processes. The first set is the average functionalities of monomers in the final polymers: this set determines local properties of gels such as their electrochemical or photochemical behavior. The second set is the exponents for the pair correlation function of all monomers in a polymer; these exponents determine whether the polymers expand throughout the whole sample volume (gels) or condense to form precipitates. Both sets indicate a continuous variation of final states between tenuous structures and dense ones.

This variation reproduces the experimental behavior. The best example is provided by TiO$_2$ based gels, where measured exponents vary from 1.6 to 3.0 according to the ratio H$^+$/Ti [13]. A similar trend from sols to gels and precipitates is shown by polymers made from cerium alkoxides modified with $\beta$ diketones, with exponents spread between 1.5 and 2.7 according to the ratio of ketone to alkoxide [17]. Even in the classical case of silicon alkoxides, the measured exponents are found to vary with pH, and they are spread between 1.7 and 2.4 [18-21].

The classical models for growth cannot produce such a variation. These models are of two families: recombination of polymers and capture of monomers by polymers [11]. Recombination of equally large polymers produces fractal structures because such polymers cannot interpenetrate; the fractal dimension depends on the particular rules for approach and sticking. In diffusion controlled aggregation of clusters (DLCA) the exponent is 1.7, and in reaction controlled aggregation of clusters (RLCA) it is 2.1. Capture of monomers by polymers produces denser structures because monomers can fill the voids of larger polymers. The exponent is 2.5 if the reactivity is high (DLA) and 3 if it is low (Eden model). This set of discrete exponents cannot describe the experimental behavior which really is a continuous variation. Worse still, the trend shown by these discrete exponents is in the wrong direction, since they predict denser structures when the overall reactivity is reduced, which is opposite from the observed behavior.

The failure of classical models comes from the fact that they take into account overall reactivity but not differences in reactivity. Such differences were introduced in the poisoned Eden model [22]; however the distribution of reactive vs. unreactive sites was random. Our model introduces a novel feature: differences in reactivity are related to local coordination. The feedback provided by this coupling allows the reaction bath to switch from one type of growth to another one. The final state results from a succession of 2 or 3 growth regimes; even though each regime may have universal features, the final state does not, because it keeps a structural memory from all the regimes which operated at some time during the growth. In this section we first identify the 3 possible modes of growth; then we examine the crossovers that allow the bath to switch from one mode to another one.

Universal regimes. — The first regime is linear growth, which starts with pairs and continues with end-to-end recombination of linear polymers. The polymers generated in this way have a fractal dimension $d_f = 1.7$. This is the exponent of linear polymers with excluded volume. In a way, this exponent was expected, since contacts between remote monomers of the polymer are counted by the model as additional bonds, and therefore treated as a departure from linear growth [23]. In another way, the result was not obvious, since the polymers are obtained through recombination of smaller polymers instead of a proper minimization of the conformations of a long chain. The agreement indicates that both procedures may be equivalent. In any case, the growth mode has universal features, since it reproduces itself at every stage of the growth.
The next regime is the random recombination of branched polymers. In this regime the growth pattern reproduces itself at larger and larger scales with a fractal dimension \( d_f = 2.1 \). This is the fractal dimension obtained with the reaction limited cluster aggregation model (RLCA) where clusters collide through Brownian diffusion and bind with a low reaction probability. Differences between our model and RLCA could have been expected at \( w \neq 1 \) since our model introduces a preference for binding on some monomers rather than others; however this selection may be prevented by steric effects when large polymers attempt to recombine. Thus the stability of our fractal dimension in this regime at \( w \neq 1 \) indicates that chemical preferences do not matter much as long as the growth occurs through recombination of equally large polymers.

Finally there comes a stage where all polymers have recombined to form a single one. If the monomers are comparatively less reactive than polymers \((w > 1)\), there will still be a collection of unused monomers in the reaction bath; then the polymer densifies by capturing the remaining monomers. For \( 1 < w < 1.6 \) the fractal dimension of the final polymer remains \(-3\); accordingly there are not enough monomers available to fully densify the largest polymer, because the densification regime starts too late, when many monomers have already been used in making polymers. When \( w > 1.6 \) the fractal dimension of the final polymer is equal to 3, but its surface is still rough: indeed the exponent of the scattering curve remains between \(-3\) and \(-4\), whereas smooth particles would give \(-4\) for this exponent [23]. This growth is universal only in the limit where the crystal grows from monomers from the start until the end; universality is reflected in the fact that the crystal shape remains stable throughout the process.

**CROSROVERS.** — The crossovers are determined by changes in the populations of reactive species. For instance branching is forced by the depletion of chain ends; densification occurs when the largest polymer finds nothing but monomers to react with. It is instructive to examine these changes in a simplified model where 2 populations are considered (free monomers and bound monomers) and 3 types of reactions are performed (free + free, free + bound and bound + bound). The steps are as follows.

a) Let \( p \) be the probability of choosing a free monomer for a coming reaction, and \( q = 1 - p \) the probability of choosing a bound monomer. These probabilities depend on the populations of either type, and on the reactivities of bound monomers; they vary during the course of polymerization.

b) The probabilities of the 3 reactions are respectively \( p^2 \), \( 2pq \) and \( q^2 \); their sum equals 1. Figure 9 presents the variations of these probabilities according to the value of \( q \). As the polymerization proceeds, the number of bound monomers increases; hence on the basis of populations alone the system should proceed smoothly to the right of the diagram. However binding also changes coordination, and therefore reactivities; this modifies the behavior of \( q \).

c) We assume that the system always performs the most likely reaction. In figure 9 this corresponds to a path along the top sections of the 3 curves: first with exclusive pair formation, then with free + bound reactions, and finally with bound + bound reactions.

d) The probabilities \( p \) and \( q \) are calculated according to populations and reactivities only; thus coordination is taken into account, but not geometry (screening effects are ignored).

Now examine the sequence of reactions at \( w < 1 \). It starts with a regime of pair formation; when the probability of selecting a bound monomer has increased beyond \( 1/3 \) it crosses over to the recombination of free monomers with the pairs already formed; the crossover time \( t_p \) is given in Appendix A. The capture of free monomers by the pairs ends when the probability of choosing a free monomer drops below \( 1/3 \); the duration \( t_m \) of this regime is also given in Appendix A.
At this point the system is a collection of oligomers, most of them triplets, together with unused monomers. The first reaction to occur beyond the second intersection is the recombination of 2 oligomers. This decreases the number of available chain ends, and it becomes more likely that for the next reaction a free monomer will be chosen to react with a chain end. Thus the system oscillates between recombination and capture, and its representative point remains locked near the second intersection of the monomer-polymer curve.

At the beginning of this regime the recombination will be end-to-end, because \( w < 1 \). This will decrease the number of available chain ends, and at some point it will become more likely that a middle chain section reacts with a chain end. This will be the onset of branching; the time \( t_e \) spent on end-to-end recombination reactions before branching is also given in Appendix A.

Beyond this point branching occurs regularly as one of the recombination reactions; the system finishes its evolution with a mixture of recombination and free monomer capture, with the relative probabilities of these reactions being determined by the selection parameter \( w \). Since the number of polymers at the onset of this regime is equal to the number of pairs formed initially, the total time spent on recombination (end-to-end and middle-to-end) is equal to the time \( t_p \) spent in forming the original pairs.

![Diagram](image)

**Fig. 9.** — Reaction rates. Horizontal axis: probability of selecting a bound monomer for a coming reaction. Vertical axis: probabilities of free + free reactions (diamonds), free + bound (hollow squares), and bound + bound (filled squares) reactions.

Figure 10 shows a diagram where the domains where each reaction is active are displayed according to \( w \) and reaction time. In this representation the polymerization of a reaction bath follows a vertical path across the diagram. Region 1 has exclusive pair formation, and its upper boundary corresponds to \( t_p \). Region 2 has exclusive monomer + pair or monomer + oligomer reactions, and its vertical extension is given by \( t_m \). Regions 3, 3' and 4 do not describe exclusive reactions but rather the length of time spent on each reaction in an
Fig. 10. — Growth diagram. The model selects a value for the chemical parameter \( w \) (horizontal axis); then growth proceeds along a vertical path in the diagram, where each region corresponds to the dominance of one growth process. Region 1: pair formation. Region 2: capture of monomers by pairs. Region 3: end-to-end recombination of pairs or oligomers. Region 3': middle-to-end recombination of oligomers or polymers. Region 4: capture of unused monomers by large polymers.

The sequence at \( w > 1 \) is similar but simpler. First, the region of end-to-end recombination has vanished. Second, because recombination increases coordination, it also increases reactivity, hence it will be the exclusive reaction until all possible recombinations have been performed. Hence region 3 corresponds to a time span during which recombination is performed exclusively, and region 4 corresponds to a final stage during which capture is the only reaction. Third, a large fraction of the time is now spent on the capture of the unused monomers, leading to substantial densification of the remaining polymer. Again, the crossover times are given in Appendix A.

6. Conclusions.

We have described a model for the growth of branched polymers or clusters through condensation reactions in solution. This model is based on a feedback between local coordination and reactivity; it allows the system to switch during its polymerization from linear growth to isotropic branching, and from isotropic recombination of branched polymers to dense growth through capture of monomers. The resulting polymers are not universal; they reproduce quite well the experimental crossover between bushy gels and dense precipitates in sol-gel processes.

At this point, it is appropriate to examine whether other rules for growth would also generate such a crossover; indeed it is important to find out whether there is more than one
way to generate dense objects through condensation reactions, and to determine which one is appropriate for sol-gel processes. There are at least 3 alternative routes to dense growth, which could be treated as extensions of this model.

a) **CONTINUOUSLY FED REACTOR.** — In our model densification is a consequence of chemical selection: polymers recombine with each other before the population of monomers is used up, and then the capture of these free monomers increases the density of the final polymer. A similar behavior may be obtained with or without chemical selection if free monomers are continuously added to the reaction bath. This is a well known receipe for making dense colloidal particles at the end of a polymerization process [24].

b) **SHORT RANGE INTERACTIONS.** — In our model chemical selection occurs at contact, because the probability of binding depends on the number of neighbors. Similar effects could result from short range forces: attraction of a free monomer by all the neighbors to a binding site would favor the growth of dense regions, whereas repulsions will favor the growth of branches. Similar effects have been demonstrated with long range forces by Meakin and Muthukumar [15].

c) **REVERSE REACTIONS.** — Our model only considers forward reactions, and the rates of these reactions are determined by energy barriers which depend on local coordination. An alternative is to assume that all binding reactions are equally likely, and introduce reverse reactions which depend on the numbers of bonds to be broken simultaneously. Then, the system will spontaneously reduce the number of poorly coordinated monomers; this amounts to taking into account the surface tension of the polymers. If the rate of these reverse reactions is high, and the binding energies are large, a nucleation barrier will appear, and clusters below a critical size will redissolve. In this way the classical nucleation and precipitation behaviors may be recovered.

**Appendix A.**

**CALCULATION OF CROSSOVER TIMES AT \( w \leq 1 \).** — First consider the pair formation regime, and assume that \( n \) pairs have already been formed. The probability of selecting a free monomer for the next reaction is proportional to their population \( N - 2n \), and that of selecting a bound monomer is proportional to \( 2nw \). These probabilities are normalized to the total reaction probability, hence:

\[
p = \frac{N - 2n}{N - 2n + 2nw}
\]

(8)

This regime ends when \( p = 2/3 \); the elapsed time \( t_p \) determines the boundary of regions 1 and 2 in figure 10:

\[
t_p = \frac{n}{N} = \frac{1}{2(1 + 2w)}.
\]

(9)

At this point it becomes more likely that free monomers will be captured by pairs. According to the model, this becomes the only reaction. Let \( m \) be the number of monomers captured during this regime; at each step the probability of selecting a bound monomer is:

\[
q = \frac{2Nt_p w + mw^2}{(N - 2Nt_p - m) + 2Nt_p w + mw^2}.
\]

(10)
This regime ends when \( p = 1/3 \) and \( q = 2/3 \); the elapsed time \( t_m \) determines the boundary of regions 2 and 3 in figure 10:

\[
t_m = \frac{m}{N} = \frac{3w}{(1 + 2w)(2 + w^2)}
\] (11)

At this point the system contains \( Nt_p \) oligomers with 2 \( Nt_p \) chain ends and \( Nt_m \) middle chain segments, and a stock of unused monomers. If \( p \) decreases below 1/3, the next reaction to occur will be the end-to-end recombination of 2 oligomers. This decreases the number of chain ends; since chains ends are the most reactive sites on the polymers, it becomes less likely that two chain ends will be chosen for the next reaction; instead, a free monomer may be chosen to react with a chain end. Thus the system oscillates between recombination and capture, and its representative point remains locked near the second intersection of the upper path in figure 9.

Let \( e \) be the number of end-to-end recombinations performed before branching occurs. The system contains \( (Nt_p - e) \) oligomers with 2 \( (Nt_p - e) \) chain ends and \( (Nt_m + 2e) \) middle chain segments. Branching occurs when it becomes as likely to select a middle chain section (probability proportional to \( w^2(Nt_m + 2e) \)) to react with a chain end (probability \( w(Nt_p - e) \)) rather than 2 chain ends. Accordingly the time spent on end-to-end recombination before branching is:

\[
t_e = \frac{e}{N} = \frac{2 - 5w^2}{2(2 + w^2)(1 + 2w^2)}.
\] (12)

This time spent on end-to-end reactions is represented in figure 10 as the extension of region 3'; it is \( > 0 \) only for \( w < (2/5)^{1/2} \); for larger values of \( w \) this regime vanishes, and middle-to-end reactions start at the same time as end-to-end, beyond the boundary of region 2.

After branching has started the system continues with a mixture of recombination and free monomer capture, but now the recombination reactions are either end-to-end or middle-to-end. Since the number of polymers at the onset of recombination is equal to the number of pairs formed initially, the total time spent on recombination (end-to-end and middle-to-end) is equal to the time \( t_p \) spent in forming the original pairs. Conversely, the time spent on free monomer capture will be:

\[
t_c = 1 - 2t_p - t_m.
\] (13)

**Calculation of Crossover Times at \( w > 1 \).** — The system starts with pairs, as above; fewer pairs are formed before the system crosses over to capture of free monomers by pairs, but the crossover time \( t_p \) is still given by formula (9); hence the boundary between regions 1 and 2 is the same.

The intermediate regime of free monomer capture is slightly more complicated because triplets may capture a monomer through a middle chain segment, which has a higher reactivity than chain ends. This will change the time span \( t_m \) to:

\[
t_m = \frac{m}{N} = \frac{1}{w(1 + 2w)} + \frac{2(-1 + w^2)}{w(-1 + 2w)(2 + w - w^2 + w^3)}
\] (14)

Further changes in the expression of \( t_m \) are needed at still higher values of \( w \) to account for
capture on sites which are 3-coordinated, 4-coordinated and 5-coordinated sites; however the corrections are small. From $w = 1.361$ to $w = 1.545$ the expression is:

$$t_m = \frac{1}{w(1+2\,w)} + \frac{1}{w(1+w)(1+2\,w)} - \frac{4 - 3\,w + 3\,w^2 + w^3}{w(1+w)(1+2\,w)(2+w-w^3+w^4)}$$

and from $w = 1.545$ to $w = 6$ it becomes:

$$t_m = \frac{1}{w(1+2\,w)} + \frac{1}{w(1+w)(1+2\,w)} + \frac{1}{w(1+w)^2\,(1+2\,w)} + \frac{-6 - 7\,w + 5\,w^3}{w(1+w)^2\,(1+2\,w)(2+w-w^3+w^4)}$$

Beyond the upper boundary of region 2 the system proceeds to recombination of all the oligomers. In this regime the probability of choosing oligomers increases as they become more highly bound, hence all oligomers are recombined before the system switches back to the capture of unused free monomers. In the representation of figure 9, the system moves to high $q$ along the polymer-polymer branch until there is only one polymer left. The duration of the recombination regime is still equal to $t_p$ because the number of polymers at the onset of recombination is equal to the number of pairs formed initially.

Finally, when all polymers have recombined, the system finds itself with one polymer and a large stock of unused monomers. The capture of these monomers is performed in region 4; it lasts for the remainder of the polymerization time:

$$t_c = 1 - 2\,t_p - t_m$$

At large $w$ values this takes up most of the total time because the early steps have been quite fast: indeed few pairs have been created in region 1, they have grown and recombined quickly in regions 2 and 3, and most of the work is in capturing the bulk of the monomers. In this sense the large $w$ limit bears some resemblance to nucleation and growth phenomena, even though there is no nucleation barrier.

References