Flory theory for the fractal nature of an irreversible kinetic gelation in branched polymers

LETTER TO THE EDITOR

Flory theory for the fractal nature of an irreversible kinetic gelation in branched polymers

R B Pandey

Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, UK

Abstract. A Flory type theory is presented for a model of kinetic gelation in branched polymers. Fractal dimensionality of the gel cluster at the gel point is estimated to be $D_f \sim [d(4x - d) + 4x]/[4x - d + 2]$ where x is the exponent for the number of monomers; this is consistent with the simulation results. It is argued that the growth in irreversible gelation is different from that in aggregation.

Recently, there has been a lot of interest in understanding the various growth processes of aggregation (Witten and Sander 1981, 1983, Meakin 1983, Ball and Witten 1984) and gelation (Manneville and de Seze 1981, Herrmann 1984 and references therein, Pandey 1984). While several theoretical attempts (Ball and Witten 1984, Witten and Sander 1983), including mean field arguments (Hentschel 1984), have been made to understand the basic features of the diffusion limited aggregation (DLA) models, the models of kinetic gelation are comparatively less explored (Herrmann 1984). Using computer simulation, Family (1983) has studied the self similarities (Mandelbrot 1982, Stanley and Coniglio 1983) of the infinite gel clusters at gel points for various radical concentrations c_i. In the two-dimensional Euclidean lattice, he found that the fractal dimensionality of the gel D_{kg} depends on c_i; in the high c_i limit it is closer to that of the percolation cluster $D_{perc} \sim 1.89$ (Stauffer 1979) and in the small c_i limit it is closer to that of DLA, $D_{DLA} \sim 1.7$. Very recently the Boston University group (private communications with Stauffer) has ruled out this claim and has shown that the fractal dimensionality of the gel cluster is similar to that of percolation for most of the concentration c_i regime. In this note we introduce simple arguments and develop a Flory type thoery (Flory 1971, de Gennes 1979, Isaacson and Lubensky 1980) to provide more physical insight into the irreversible kinetic gelation model which suggests that kinetic gelation and aggregation are quite different growths.

The basic idea behind the simplified model considered here is very simple. In computer simulation models (Manneville and de Seze 1981, Herrmann 1984, Pandey 1984), the lattice sites are first filled by monomers; radicals are then placed on a small fraction c_i of these sites. Reactions are grown by adding bonds at the trajectories of the random walk motion of growth (active) centres; a bond may join two monmers, a monomer and a cluster (the macromolecule) and two clusters. The return of the random walker (the radicals) to its previously visited sites (monomers) is restricted due to restricted functionalities (i.e. the number of bonds by which the site can be connected to its neighbouring monomers). The active centres (radicals) can be trapped

if all its neighbouring monomers are saturated; when two active centres meet they may annihilate each other. There are several variants of this growth model, for example, conserving the concentration of radicals (Pandey 1984), constantly increasing the concentration of radicals during the reaction growth (Mathews-Morgan and Landau 1984), etc (some other growths may be found in Pandey (1984)). Increasing the functionalities by considering high functional monomers in the sol phase, the restriction on return of the random walk mentioned above can be reduced drastically and so is the chance of trapping. Furthermore, increasing the functionalities does not change the qualitative nature of the phase diagram (Pandey 1984). If one considers the growth of kinetic reaction via a small concentration of active centres, then the chances of their encounter (and therefore the chances of annihilation) may be reduced. We therefore consider the growth of kinetic gelation by growing the bonds at the simple unrestricted random walk trajectories of the active centres, using the approximation of neglecting the annihilation.

Let there be N monomers (sites) in the gel network at the gel point; these are the number of distinct visited sites say in time t (since a site can be visited more than once and therefore a monomer can be connected by more than one bond to its adjacent monomer) for which (Montroll and West 1979)

$$N \sim t^{1/2} \qquad d = 1$$
$$\sim t/\ln t \qquad d = 2$$
$$\sim t \qquad d = s \text{ with } s \geqslant 3 \tag{1}$$

where t is approximately a measure of the number of grown bonds. The root mean square displacement (end to end distance) is given by

$$R_{\text{RMS}} \sim N^{1/2x} \tag{2}$$

where $N \sim t^x$ ($x = \frac{1}{2}$ for $d = 1$ and $x = 1$ for $d \geqslant 3$). One must note that the following analysis is valid only for $d = 1$ and $d \geqslant 3$, where this simple power law is applicable. Since the radius of gyration of the cluster is proportional to the RMS displacement, the elastic free energy (entropic contribution) is given by (de Gennes 1979)

$$F_{\text{el}} \sim R^2 N^{-1/x}. \tag{3}$$

To estimate the repulsive free energy, we recall the history of the growth. The whole network is made up of blobs; each blob is a cluster formed by the random walk motion of an active centre. Let there be n_b blobs. n_b is of the order of the number of active centres in the reaction growth,

$$n_b \sim c_i R^d. \tag{4}$$

On average, there are N_b monomers per blob with

$$N_b \sim N/n_b \sim NR^{-d}/c_i. \tag{5}$$

If the radius of gyration of a blob is R_b, then the intrablob repulsion free energy is given by

$$F_{\text{intra}} \sim N_b^2/R_b^d \sim N_b^{2-d/2x}$$
$$\sim N^{(4x-d)/2x} R^{-d(4x-d)/2x} \tag{6}$$

and the interblob repulsion free energy by

$$F_{\text{inter}} \sim n_b^2 / (R/R_b)^d \sim N^{1/2x} R^{d-d/2x}. \tag{7}$$

Therefore, the total free energy is

$$F = F_{\text{el}} + F_{\text{intra}} + F_{\text{inter}}.$$
$$\simeq R^2 N^{-1/x} + N^{(4x-d)/2x} R^{-d(4x-d)/2x} + N^{1/2x} R^{d-d/2x}. \tag{8}$$

Now the equilibrium radius of gyration can be estimated from

$$\partial F / \partial R = 0. \tag{9}$$

Keeping all the terms in the free energy (equation (8)), it is not possible to find a closed form expression for the radius of gyration R_g. We may, however, analyse the contribution of each repulsion term separately. If we neglect the intrablob repulsion and consider only the interblob repulsion with the elastic attraction term, then we get the results for the radius of gyration R_g which do not seem physical. On the other hand if we neglect the interblob interaction and consider only the intrablob repulsion, then criterion (6) gives

$$R^{[d(4x-d)+4x]/2x} \sim N^{(4x-d+2)/2x} \qquad \text{for } (4x-d) > 0. \tag{10}$$

Using the definition of the fractal dimensionality D_f,

$$R^{D_f} \sim N, \tag{11}$$

we obtain

$$D_f = [d(4x-d)+4x]/(4x-d+2) \qquad \text{for } (4x-d) > 0. \tag{12}$$

This gives $D_f = 1$ for $d = 1$ and $D_f \approx 2.3$ for $d = 3$. Note that (12) is an approximate result, and to find an accurate estimate one has to take into account all relevant interactions in appropriate proportions, then, as we have seen above, it is not feasible to obtain a closed form expression for D_f.

In $d = 2$ Euclidean space the situation is very complex because of the logarithmic dependence of the number of distinct visited sites (i.e. monomers) in time t (equation (1)). Let us see what can we say about the fractal dimensionality of the gel network in this case. We assume an exponent z for the logarithmic dependence of N on t such that

$$t \simeq N \ln^z t \simeq N \ln^z (N \ln^z N \ln^z \ldots)$$
$$\simeq N \ln^z N \qquad \text{(to leading order).} \tag{13}$$

Then the entropic contribution to the free energy may be written as

$$F_{\text{el}} \sim R^2 / (N \ln^z N) \tag{14}$$

where $R_{\text{RMS}} \sim N^{1/2} \ln^{z/2} N$ is used. The intrablob free energy may then be obtained from (6) and (13),

$$F_{\text{intra}} \sim N_b^2 / R_b^d \sim N^{(4-d)/2} R^{d(d-4)/2} [\ln (NR^{-d})]^{-zd/2}. \tag{15}$$

Note that these relations are valid only for $d = 2$. As in our previous analysis, the free energy F may be obtained by adding (14) and (15). The equilibrium condition (9) then gives

$$R^{(4+4d-d^2)/2} \sim N^{(6-d)/2} \ln^z N [\ln(NR^{-d})]^{-zd/2} [d(4-d)/2 - (zd^2/2)(\ln(NR^{-d}))^{-1}]. \tag{16}$$

One can easily check that, in the absence of logarithmic dependence here, the fractal dimensionality D_f is equal to 2 and that the logarithmic correction reduces it to $2 - \varepsilon$, where ε is a correction. Such a logarithmic correction was noted also in percolation studies (Stauffer 1981). Although we are unable to provide a precise value of this correction, our crude analysis presented here does give an idea about the fractal nature of the gel model. Our results for the fractal dimensions are in qualitative agreement with those of computer experiments; these are compared in the table.

Table 1. D_{kg} (experiment) are the values from Herrmann *et al* (1983) and Pandey (1984) and D_{kg} (theory) are from our approximate theory.

d	D_{kg} (experiment)	D_{kg} (theory)
1	1	1
2	1.8	$2 - \varepsilon$
3	2.5	2.3

Based on the approximate analysis, the following qualitative picture emerges: the gel network is made up of blobs which are interpenetrating each other very strongly, while each blob within itself is very repelling. As a result, the network looks less dense within the blob and highly dense and crosslinked at their intersections; a qualitative picture is shown in figure 1. Thus, in contrast to DLA clusters which are opaque to the diffuser, the gel clusters are most likely to be transparent.
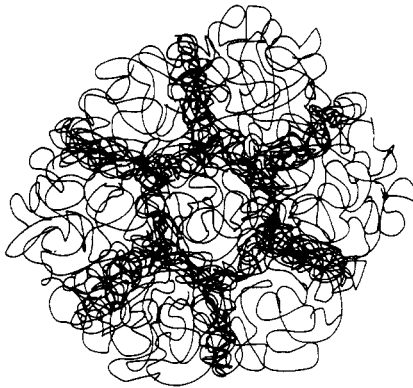

Figure 1. Qualitative picture of a model network.

References

Ball R C and Witten T A 1984 *Preprint, Particle aggregation versus cluster aggregation in high dimensions*
de Gennes P G 1979 *Scaling Concepts in Polymer Physics* (Ithaca: Cornell University Press)

Family F 1983 *Phys. Rev. Lett.* **51** 2112

Flory P 1971 *Principles of Polymer Chemistry* (Ithaca: Cornell University Press)

Hentschel H G E 1984 *Phys. Rev. Lett.* **52** 212

Herrmann H J 1984 invited talk at *Int. Conf. on Kinetics of Aggregation and Gelation, Athens, Georgia April 2–4*

Herrmann H J, Stauffer D and Landau D 1983 *J. Phys. A: Math. Gen.* **16** 1221

Isaacson J and Lubensky T C 1980 *J. Phys. Lett.* **41** L469

Mandelbrot B 1982 *The Fractal Geometry of Nature* (San Francisco: Freeman)

Manneville P and de Seze L 1981 in *Numerical Methods in the Study of Critical Phenomena* ed I Della Dora, J Demongeot and B Lacolle (Berlin: Springer)

Mathews-Morgan D and Landau D 1984 to be published in *Phys. Rev. B*

Meakin P 1983 *Phys. Rev. A* **27** 1495

Montroll E W and West B J 1979 in *Fluctuation Phenomena* ed E W Montroll and J L Lebowitz (Amsterdam: North-Holland).

Pandey R B 1984 *J. Stat. Phys.* **34** 163

Stanley H E and Coniglio A 1983 *Ann. Israel Phys. Soc.* vol 5 *Percolation Structures and Processes* ed G Deutscher, R Zallen and J Adler (Bristol: Adam Hilger)

Stauffer D 1979 *Phys. Rep.* **54** 1

—— 1981 *Phys. Lett.* **83A** 404

Witten T A and Sander L M 1981 *Phys. Rev. Lett.* **47** 1400

—— 1983 *Phys. Rev. B* **27** 5686