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# A simple model of the polymerisation process

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**Abstract.** The monomer is taken to be a fluid with purely repulsive interactions, which is treated by the Mayer theory. Some of the repulsions between pairs of monomer molecules are modified to become strong attractions by the assumed polymerising agent; and the gelation point is taken to be determined by the pressure passing through a maximum with increasing density.

If the repulsions are taken to be Gaussian, detailed calculations can be made and it is found that the position of the gel point is little affected by correlations between the pairs of molecules whose interactions are modified.

## 1. Introduction

We suppose the raw-material monomer to be an assembly of effectively spherical molecules and, for simplicity, we assume that they exert purely repulsive central forces on one another. The monomer molecules are now supposed to be modified by whatever agent causes the polymerisation, for example heat, irradiation or chemical treatment, so that the interactions between some of the pairs of molecules are changed from repulsive to attractive, the remaining interactions remaining repulsive. We are interested in predicting the expected structure of the polymer, that is to say the amount of branching of the polymer chains and the conditions that lead to gelation. It turns out that they are both related fairly simply to the parameters that describe the original and the modified interactions.

It is physically obvious that the structure of the polymer must depend critically on the number of other molecules with which a typical one is interacting, that is on the mean 'valency'. If it is one we can only have dimers, if it is two we shall have linear chains. If it is more than two, we shall have branched chains and ultimately expect cross-linking and gelation. We shall first examine the consequences of the assumption that the intermolecular interactions are modified in a completely random fashion using some of the results of Erdös and Renyi (1960) on random graphs. It is also possible to work out the consequences of an opposite extreme assumption, namely that the modifications of the interactions are so strongly correlated that no monomer can attract more than two others. This constrains the polymer molecules to be linear, but seems to have very little effect on the gelation point. Indeed the predictions are largely independent both of the precise assumptions made and of the detailed behaviour of the virial coefficients of the monomer.

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## 2. Description of the model

We describe the monomer by means of the treatment by Mayer and Mayer (1940) of the classical imperfect gas. The equilibrium configuration partition function is obtained (to a factor) by integrating the following quantity (actually the Boltzmann factor for the whole assembly over all the possible positions in the vessel of all the $N$ monomer molecules present.

$$\text{Integrand} = \prod_{ij} (1 + f_{ij}). \tag{1}$$

Here $f_{ij}$ is the Mayer function $\exp(-V_{ij}/kT) - 1$ describing the interaction $V(r_{ij})$ between monomers $i$ and $j$, and is a function of the distance $r_{ij}$ and of the temperature. For a purely repulsive interaction $f$ will be negative everywhere; near to $-1$ for $r = 0$ and falling to zero in a distance of a few molecular diameters. As we are mainly concerned with the low-density region we are not concerned with the now well known fact that even a purely repulsive interaction can, at sufficiently high density, induce a transition resembling solidification.

We choose for $f$ the Gaussian function

$$f_{ij} = -\exp(-r_{ij}^2/a^2) \tag{2}$$

because (Uhlenbeck and Ford 1962) it is possible to calculate any assigned Mayer cluster integral explicitly. It is easy to modify the theory for other types of purely repulsive interaction. For example, for rigid spheres of diameter $a$ we have, in place of (2), a function $f$ that is $-1$ for $r < a$ and zero for $r > a$.

We now suppose that, as stated above, a fraction $p$ of the inter-monomer Boltzmann factors are modified in this way

$$1 + f \to A|f| \tag{3}$$

where $p$ is small and $A$ is large. In words, for a small fraction of the pairs of molecules a weak repulsion is replaced by a strong attraction. Of course there is no physical reason why we should have the same function $f$ on both sides of (3), but we do expect the ranges of the attractions and repulsions to be of the order of a few molecular diameters and retaining the form of $f$ is very convenient mathematically.

### *Assumption* A

Assumption A, whose consequences we now develop, using (2) and (3), is that the interactions between the $\binom{N}{2}$ pairs of molecules are modified completely at random. We assume further that, after the modifications, we wait for the assembly to come to a new state of statistical equilibrium. Therefore, we average over *all* possible choices of bonds that are to be modified in the sense (3), each having a probability $p$ of being modified. We can calculate the new partition function by replacing $1 + f$ in (1) by $(1-p)(1+f) + pA(-f)$ (remember that $f$ is negative). For the Gaussian interaction (2) the factors $1 - \exp(-r^2/a^2)$ in (1) are replaced by factors

$$(1-p)\left(1 + \frac{pA + p - 1}{1-p} \exp(-r^2/a^2)\right). \tag{4}$$

Thus, apart from the numerical factor $(1-p)^{\binom{N}{2}}$ the integrand for the modified assembly remains of the same form as (1), but with a different numerical coefficient for the

exponential. Therefore, we can still use the Mayer theory, and we now investigate what happens when the coefficients of the exponentials become positive, as they do when $p$ becomes large enough.

## 3. Consequences of assumption A

Consider first of all the critical case $p = 1/(A+1)$.

The integrand is no longer a function of the $r$'s and, apart from the factor $(1-p)^{\binom{N}{2}}$, the configuration partition function becomes just $V^N$ (as for the perfect gas) because the effects of attractions and repulsions balance, so that every molecule can reach everywhere in the volume $V$ with the same probability. This critical value of $p$ is reminiscent of, but *not* identical with, the so-called 'theta-point' defined by Flory. This arises, for a polymer in solution or in equilibrium with its monomer, as follows. The possible configurations of any chain are restricted by the effect of repulsions between non-neighbouring segments of the chain. The effect of these can be balanced, to a first approximation, by a net attraction between the segments and the solvent or the monomer molecules. In fact, the 'theta-temperature' is quite analogous to the Boyle temperature of an imperfect gas, e.g. the van der Waals gas. There is an approximate balance between the effects of the short-range repulsion and the longer-range attraction between pairs of molecules, so that we have the real gas nearly obeying the perfect gas laws near the Boyle temperature. It must be stressed that, in this model, the balance is associated with the probability $p$, rather than with the temperature, since temperature cannot really be defined for a Gaussian model. We have only an analogy with the Boyle temperature and the Flory theta-point, nothing more.

We shall show that an assembly whose effective pair Boltzmann factor is of type (4) can still sustain an external pressure even if the factor $q = (pA + p - 1)/1 - p$ is positive, provided that it is not too large. How large can it be? We can answer this by applying the Mayer theory with an effective Mayer function $q \exp(-r^2/a^2)$, the factors $(1-p)$ in (4) not affecting the pressure. We can calculate the virial series as in Temperley (1977) which studied the Gaussian model of the imperfect gas with $f$ negative. We use the same technique of splitting the virial series into sub-series, in each sub-series grouping together irreducible diagrams which have the same cyclomatic number. This grouping has the advantage that all the sub-series have the same radius of convergence $x = 1/qb$. Repeating the work of Temperley (1977) with $q$ positive we find, after correcting some obvious misprints in that paper,

$$\frac{P}{kT} = x - \sum_k \frac{k\beta_k}{k+1} x^{k+1} \tag{5}$$

$$= \underset{\text{(Perfect gas)}}{x} \underset{\text{(Pairs)}}{- \tfrac{1}{2} qbx^2} - \tfrac{1}{2}\left(\frac{2q^3}{3}\frac{x^3 f^2}{3^{d/2}} + \frac{3q^4}{4}\frac{x^4 f^3}{4^{d/2}} + \ldots\right) - \tag{6}$$

with further negative terms for $\theta$ graphs, etc. where all terms except the first are negative and where $x = N/V$, $b = (\sqrt{\pi}\, a)^d$, $d$ = number of dimensions (for $d = 2$ the ring series contribution to $\partial P/\partial x$ sums in closed form, but we do not need this result here).

The consequences of (6) now follow very easily. For small $x$, the pressure is positive, but it goes through a maximum just below $x = 1/qb$ and quickly plunges to

unphysical negative values. The contributions of the higher graphs are all negative and each subseries diverges exactly at $x = 1/qb$. We conclude that the pressure maximum is unstable and that at any higher pressure the assembly would collapse to a smaller volume (theoretically zero because the cores are soft). We identify the corresponding critical value of $p$ with the onset in gelation, which takes place once we go past the maximum of $P$.

## 4. Some properties of a random graph

Contrary to intuition, Erdös and Renyi (1960) have shown that a completely random choice of some of the $\binom{N}{2}$ lines of a complete graph on $N$ points has asymptotically some very definite structural features, which appear in five different stages. To get long linear chains, one clearly needs an expected number of links comparable with $N$. The first two of Erdös and Renyi's stages are as follows. Let $L$ be the expected number of links in the polymer (that is bonds that have been changed to attractive ones.) We consider the graph formed by these links.

(*a*) $L = 0(N)$. Graphs mainly trees

(*b*) $L = (\frac{1}{2} - \alpha)N$. Largest tree contains about $2 \ln N/\alpha^2$ points. If $\alpha$ becomes zero, a well-marked transition occurs and the largest tree now contains about $N^{2/3}$ points, so that each point has a valency of the order of $N^{1/3}$. This is not realistic for any polymer. Therefore, we must keep $L$ below $\frac{1}{2}N$, but only just below it, otherwise we shall get short polymers. Quantitatively, we must take $\alpha^2$ of the order $\ln N/N$ to make the number of vertices comparable with the number of edges, and this implies that $A$, the ratio of attractive to repulsive Boltzmann factors, is of the order $N/\ln N$. A large ratio between a chemical and a physical interaction is not unreasonable, and below we shall show that a dependence on $N$ is also reasonable.

## 5. Removal of assumption A

Chemically, we would not expect more than about four linkages per monomer for steric reasons. So, if $L$ is greater than $N/2$, we can no longer modify our bonds at random, but must introduce some correlation which has the effect of limiting the valencies of our graphs. (At present, we do not have the generating function for all graphs with maximum valencies of three or four.)

We can, however, examine fairly easily the consequences of two assumptions that are, in a sense, the exact opposites of assumption A. There are now strong correlations or anti-correlations between the various attractions that can be introduced.

### *Assumption B*

The graphs corresponding to the introduction of factors like (4) have a maximum valency of one, that is to say are simply dimers and monomers. This means that, for example, no more than one of two factors like $(1+f_{12})$ and $(1+f_{23})$ that have a suffix in common can be modified. The monomer–dimer generating function can be precisely written down for the complete graph on $N$ points which means that we can list all permissible modifications of the Mayer terms.

We find that the first two terms of the virial series are the same as in (6) but that no more than half of the interactions in a ring term can be modified, the others remaining negative. Therefore, the various possibilities will all lead to ring-type series smaller in numerical magnitude than the terms in (6) and with terms of mixed signs. Now for a virial series of the form (6) we have already found that the position of the gelation point is mainly determined by the first two terms, $x$ and $-\frac{1}{2}qx^2b$, the ring and higher terms having little effect apart from shifting the maximum of $P$.

*Assumption C*

Graphs corresponding to the introduction of attractions are of valency 2 at most. Again, the generating function for such graphs is precisely known, since the only such graphs are dimers, chains and rings, and we know in exactly how many ways a set of $l$ points can be connected up into a ring or chain. In this case, in the virial we have the terms $x$ and $-\frac{1}{2}qbx^2$ as in (6) but now it *is* possible to have ring terms all of the same sign. Again the predictions are similar to those of (6). Therefore, whether we assume that the probabilities of two neighbouring Boltzmann factors such as $(1+f_{12})$ and $(1+f_{23})$ being modified are independent (assumption A), strongly anti-correlated (assumption B) or strongly correlated (assumption C), we get very similar predictions of the value of $x$ for which $\partial P/\partial x = 0$.

One may wonder how assumption B can produce 'gelation'. What it really predicts is that, given a strong enough attraction, a typical dimer collapses to a very small volume if the pressure is high enough. The less artificial assumptions A and C predict that the collapse of a whole chain or ring takes place under about the same conditions as that of a dimer, which is reasonable.

## 6. Discussion

It seems artificial to have to assume that, according to assumption A, the number of attractive links introduced is only very slightly less than $\frac{1}{2}N$. The corresponding assumption that $A$, the relative strength of the attraction is large is quite plausible, but it seems, at first sight, unsatisfactory in that it also has to be a function of $N$. This is probably the result of assuming no correlations at all between the introduced attractions. The situation is very similar to that of the Weiss ferromagnetic or the van der Waals gas. In these theories the consequence of assuming that the interaction between a pair of molecules is independent of distance is that, in order to get sensible physical results, we have to take its strength as proportional to $1/N$.

It is of interest that the onset of gelation, or the collapse of chains, seems to be very largely independent of the model.

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