SOL-GEL TRANSITION

Antonio Coniglio

G.N.S.M. and Istituto di Fisica Teorica, Mostra d'Oltremare Pad. 19,
80125 NAPOLI, ITALY (permanent address)

and

Center for Polymer Studies Boston University, BOSTON, MA 02215, U.S.A.

Abstract

The basic phenomenology of the SOL-GEL transition is reviewed. Distinction is made between reversible and irreversible gelation, which can be interpreted correspondingly as an annealed and quenched process. The geometrical nature and the driving mechanism of the SOL-GEL transition is described and analogies and differences with other types of phase transitions are pointed out. Classical theories, which neglect loops predict a set of critical exponents rather different from those predicted by percolation models. However more realistic kinetic models seem to fall even in a different universality class. When solvent effects are taken into account, the occurence of critical density fluctuations gives raise to interesting multicritical phenomena, which can be described by a lattice gas Potts model. The structure of the gel network in the vicinity of such multicritical point is predicted to be rather different from the usual one.

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1. - Introduction

The basic theory for the SOL-GEL transition, based on the appearance of an infinite molecule, was originally proposed by Flory and developed in a series of classical papers by both Flory[1] and Stockmayer[2]. More elaborated models have been introduced later. They are all based on "connectivity" as the key mechanism to explain such transition. In this talk I will review the basic phenomenology and describe the different models of the SOL-GEL transition, stressing the analogies and differences with the more familiar thermal transitions such as the liquid-gas.

2. - Basic Phenomenology

The SOL-GEL transition is characterized by a drastic change in the viscoelastic properties of the system (for general reviews see Refs. (3) - (7)). In the sol-phase the viscosity is finite, while in the gel-phase is infinite and like a solid can sustain a shear stress. At the transition point the viscosity η diverges coming from the sol-phase and the elastic shear modulus E goes to zero, coming from the gel-phase.

To describe the process from a microscopic point of view we consider the simplest case of gelation, the polyfunctional condensation of f-functional monomers. Suppose that all the monomers are identical and that each has f-functional groups then can react with one of the f-groups of another monomer. For f > 3 the system develops branched polymer.

A characteristic parameter is the conversion factor p, which is the fraction of reacted groups. If p = o only monomers are present, for p = 1 all the monomers form one macroscopic "infinite" molecule. (Of course the macromolecule is infinite only in the thermodynamic limit). There is a critical value p_c, such that for $p < p_c$ only finite molecules (also called "clusters") are present. This is the "sol" phase, while for $p > p_c$ an infinite molecule ("gel" phase) is present coexisting with finite molecules.

3. - Relevant Quantities and their Exponents

We now define the quantities of interest and the corresponding exponents which can be measured near the gel point, or which have been studied using theoretical gelation models. The mass s of an s-cluster is the number of monomers in such a macromolecule. Assuming scaling, the average number $n_s(p)$ of s-clusters per monomer is

$$n_s(p) \sim s^{-\tau} f(\varepsilon s^{\sigma}) \qquad (s \to \infty, \varepsilon \equiv \frac{p - p_c}{p_c} \to o),$$

the weight average (or the mean cluster size) degree of polymerization DP is defined as

$$DP = \frac{\Sigma' s^2 n_s}{\Sigma' s n_s} \propto |\varepsilon|^{-\gamma}.$$

Σ' denotes the sum over all finite clusters but excludes the infinite cluster. For simplicity we will assume always the same critical exponents on both sides of the phase transition.

The gel fraction G which is zero for p below p_c is

$$G = 1 - \Sigma' n_s \propto \varepsilon^{\beta} \qquad p > p_c.$$

The probability p(r) that two monomers at distance r belong to the same cluster

$$p(r) \sim \frac{g(r/\xi)}{r^{d-2+\eta}}.$$

ξ is the typical cluster radius which diverges at the gel point as

$$\xi \propto |\varepsilon|^{-\nu} ,$$

all these exponents β , γ , η , ν can be expressed in terms of σ and τ only[8],[9].

The existence of a characteristic diverging length ξ , an order parameter continuously vanishing at the gel point, a strongly diverging quantity DP, related to the fluctuation of the order parameter[10], makes the SOL-GEL transition similar to ordinary thermal phase transitions, such as the liquid-gas transition.

We note that in thermal phase transitions, the thermal fluctuations are the driving forces for critical behaviour. In the SOL-GEL transition the mechanism leading to critical behaviour is purely geometrical. To visualize this mechanism imagine to be just below p_c. The cluster distribution is characterized by large clusters of linear dimension ξ . As p increases by a small amount δ p , many of these clusters coalesce, giving rise to much larger clusters whose linear dimension is increased in a highly non-linear way. It is this non-linear response which leads to critical phenomena.

4. - Classical Theory of Gelation

The classical picture for gelation was proposed more than 40 years ago.[1][2] This is based on the assumption that no cycles are formed in the molecules. Nowadays we recognize this as the "Tree" approximation of the percolation model[11] which will be discussed in the next sect. This approximation leads to mean-field exponents which in percolation are valid only above the upper critical dimensionality d_c = 6.

5. - Percolation Model

We recognize that the essential feature of this gelation process is connectivity and hence we expect that percolation models[12[13] would be suitable in describing such transition. I will describe first the standard random-bond percolation[8][9] which is relevant to gelation in absence of solvent. (See Sect. 9 for a generalization of this model to incorporate solvent effects).

In the percolation model monomers occupy the sites of a lattice. Between two nearest neighbours of lattice sites, a bond is formed with a random probability p (Fig. 1, a, b).
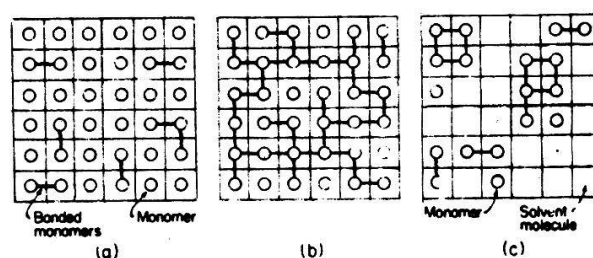
Fig. 1

Every bond configuration is characterized by a cluster distribution (molecules). Since the bonds are independent of each other the weight of a given configuration of n bonds is given by $p^n(1-p)^{N-n}$ where N is the maximum number of bonds in the lattice. For small p the system consists of small clusters. As p increases the average size of a cluster increases and diverges at the percolation threshold p_c. This point is characterized by the onset of an infinite cluster. Above p_c an infinite cluster is present.

In this model the number of s-clusters n_s is associated to the molecular distribution in the gelation problem. From the connectivity properties of the percolation problem one can calculate all the quantities of interest except for the viscosity and the elastic modulus. One needs additional theories to calculate them.

It has been suggested[14] that the viscosity diverges at p_c like the conductivity in a random mixture of superconductors (fraction p) and normal conductors (fraction 1-p); while the elastic modulus goes to zero at p_c as the conductivity of a random mixtures of conductors (fraction p) and insulators (fraction 1-p). There have been many attempts to relate these exponents to other percolation exponents. In particular for the conductivity exponent t it has been suggested[15] the following relation $t = \frac{1}{2} |\nu(3d-4)-\beta|$ which seems to be rather well satisfied numerically.

Let us mention however that recently the analogy between conductivity and elasticity has been questioned.[21] Instead it has been proposed that the elastic constant varies as $\xi^{-d} \propto \epsilon^{\nu d}$.

6. - Cluster Structure Near the Gelation Threshold

One of the main problems, not yet fully solved, is the knowledge of structure of the network, since many macroscopic properties, such as the elastic constant depend on it. In a network one has to distinguish between "dangling" bonds or dead ends which do not contribute to the elasticity, and

the backbone bonds which are all the others.

Recently some progress has been made in understanding the structure of the backbone in the percolation model based on exact results[16]. It is found that just below p_c, the backbone of the typical cluster of linear dimension ξ
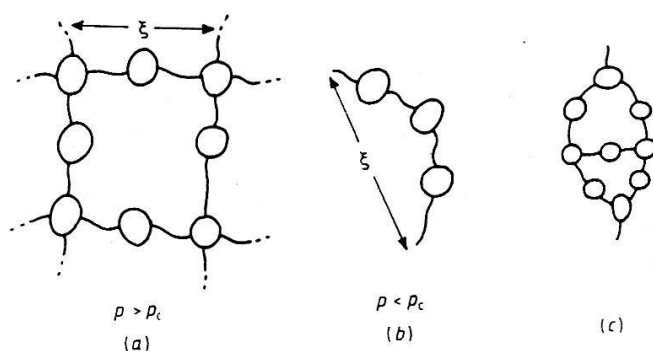

Fig. 2

is made of cutting bonds or links such that if one is cut the cluster breaks in two parts, and all the others which lump in "blobs". The number of links N_{links} diverges in any dimension with an universal exponent 1, $N_{links} \propto \varepsilon^{-1}$. A result which has been confirmed by Monte Carlo methods for d = 2[17]. The number of the other bonds N_B diverges with a dimensionality dependent exponent Z_B, $N_B \propto \varepsilon^{-Z_B}$. The structure is self-similar for length scale less than ξ. This result suggests that above p_c the backbone of the network is made of "nodes links and blobs", instead of "nodes and links"[18]. The observation that the bonds may be partioned in links and blobs was originally made by Stanley[19].

7. - Comparison between Classical Theory and Percolation Model

The view that the percolation model describes the SOL-GEL transition better than the classical theory (at least in the critical region) is far from being universally accepted. A comparison of the main predictions is given in Table I. For more details see Ref. (6).

Unfortunately the experimental data are not so accurate in the critical region. In particular it is very hard to determine p_c. This in turn gives a large indetermination on the exponents. However recently Schmidt and Burchard[20] analysed the light-scattering data and the weight data of the gel fraction and used the relation $\xi \propto G^{-\nu/\beta}$, $DP \propto G^{-\gamma/\beta}$, in this way they got rid of p_c and extracted ν/β and γ/β which take rather different values in the competing theories, and a better comparison is possible. From table I the experiments seem to agree better with the percolation model.

TABLE I

	Experiments	Classical Theory	Percolation Model (d=3)
β		1	0.45
γ		1	1.7
ν		0.5	0.88
ν/β	1.65~3.3	0.5	2
$\gamma\,\beta$	4 ~ 5	1	4

The values for the percolation model are the best numerical data from Ref. (6)

8. - Free-Energy Singularities: Reversible and Irreversible Gelation

In thermal phase transitions we know that the free energy has singularities at the critical point. A question which recently has received some attention[21] is whether the gel transition is accompanied by a free-energy singularity. In order to answer such question we have to distinguish between reversible and irreversible gelation.

<u>Reversible gels</u> are characterized by the fact that the bonds are not permanent and they can form and break in thermal equilibrium (annealed). As discussed in more details in Ref. (21) the "annealed" free energy does not show any singularity at the percolation threshold. The gel phase is more similar to a highly viscous liquid, with strong analogies with the glass transition[14].

<u>Irreversible gels</u> are characterized by permanent bonds (quenched). To be more precise for a given distribution of bonds the system is made of different species of molecules (monomers, dimers...). The free energy of such system averaged over all possible bond configurations has been estimated[21] and exhibits the same singularity as the average number of clusters $F_{sing} \propto \varepsilon^{2-\alpha}$.

9. - Solvent Effects

In the random percolation model presented in Sect. II, no solvent was taken into account. A more general model, the site-correlated random-bond percolation[22], has been introduced to take into account solvent effects, which may strongly influence the gelation process. In this model (Fig. 1c)

i)   every site can be occupied either by a monomer or by a solvent molecule;

ii) the monomers are not randomly distributed, instead it is assumed a correlation of the standard lattice-gas model. Finally random bonds between nearest-neighbor monomers with a temperature-dependent probability are assumed.

To study the gelation process we have to distinguish again between rever-
sible and irreversible gelation.

In reversible gelation the bonds are not permanent,therefore the monomers
keep their individuality. The thermal properties are obtained solving the
lattice-gas model, the well-known phase diagram shows a consolute temperature
T_c below which the phase will separate into two phases like in an ordinary
binary mixture (Fig. 3).

The gelation line, which separates the sol-phase from the gel-phase, is
instead given by the percolation threshold in this site-correlated random-
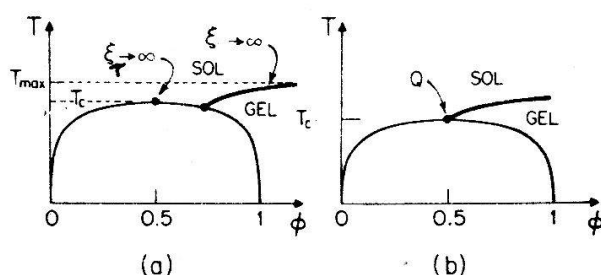bond percolation. It is interesting to note that by changing solvent one can

Fig. 3   (a)   (b)

realize the interesting situation in which the critical line ends on the con-
solute point, which corresponds to a higher-order critical point, where both
the thermal correlation length, and the connectedness length diverge Fig.(3b).
Along this critical line the gelation process is characterized by random-per-
colation exponents, with a crossover to lattice-gas exponents at the consolute
point. This shows that the large density fluctuations in the vicinity of the
consolute point strongly influence the gelation process.

These results have been found using the Migdal-Kadanoff renormalization
group[23], ε-expansion[24] and Monte Carlo[25]. There are no experimental data
to confirm this crossover effect, however the phase diagram in the case of
polymer gelation[22], is in agreement with the experimental results of Tanaka
and coworkers[26]. It is interesting to note that the phase diagram of Fig.(3)
has strong analogies with other phase diagrams of completely different systems,
such as the λ-line in the He 3 -He 4 mixture[27], the phase diagrams of adsorb-
ed systems such as krypton on graphite[28], branched polymer in a solvent[29].

These analogies are not surprising, in fact all these systems can be de-
scribed by the dilute s-state Potts model for different values of s (Table IV),
which all have similar phase diagrams[30].

TABLE IV	System	Model	Dilute s-state Potts
	branched polymer in solvent	site-correlated random-bond animal (Ref.29)	0
	gel in solvent	site-correlated random-bond percolation (Ref.22)	1
	λ-line He3-He4	Blume Emery Griffiths (Ref.27)	2
	Krypton-adsorbed on graphite	Berker Ostlund Putman (Ref.28)	3

Irreversible gels are obtained from the monomer solvent mixture, by forming quickly a fraction of permanent bonds, at a quenching temperature T_Q. Once these bonds have been created the system no longer consists of single monomers but of permanent clusters (monomers, dimers, trimers, possibly including an infinite polymer network). Later the temperature may change inducing even first-order transition[31] (gel collapse), but the cluster distribution will always be the same independent of the varying thermodynamic temperature. An interesting aspect of strong gels, which has not received much attention experimentally, is that quenching (bond formation) occurs exactly at the critical consoled point. In this case the resulting size distribution of macromolecules is permanently influenced by the highly correlated distribution of monomers (although the consolute point may be shifted after the bonds have been formed, due to the presence of large molecules[32]). In particular if an infinite network is formed, it should exhibit unusual elastic properties about which little is known at present.

7. - Branched Polymers

Let us consider the polymerization process described in Sect. 2 in the very dilute limit where the molecules do not interfere with each other. In this case we can consider the growth of only one isolated branched polymer. The quantity of interest is the radius of gyration R_s of an s-molecule as function of s, $R_s \propto s^\rho$. A model for branched polymer is given by a single cluster, also called lattice animal[9][34][35]. This corresponds to the very dilute limit of the percolation problem. Recently crossover from percolation to lattice animal has beeen described.[33]

A suitable model for branched polymer in a solvent is a lattice animal in

which the monomers interact with a nearest-neighbor interaction. This corresponds to the dilute limit of site-correlated randombond percolation, and can be obtained in the s = o limit of the dilute s-state Potts model[29]. Migdal-Kadanoff Renormalization group[29] and ε-expansion[36] give for this system the following critical behaviour: (i) Random lattice animal, (ii) θ or collapse. (iii) percolation. (iv) compact. The behaviour (i), (ii), (iv) are similar to that of a linear chain in a solvent. The percolation behaviour is present only in branched polymers. This corresponds to a higher-order critical point where the effect of the solvent is identical to the screening effect due to the presence of the other clusters in the percolation problem.

8. - Kinetic Models

In the percolation model a strong assumption is the complete randomness of bond formation. This corresponds to the rather ideal situation where the bonds are formed instantaneously and at random. In reality the bond probability may depend on the particular kinetics involved in the cluster formation. A frequently used kinetic equation[37][38], based on Smoluchowski's coagulation equation is the following

$$\frac{dn_s}{dt} = \sum_{s'+s''=s} K_{s's'} \, n_{s'} \, n_{s''} - n_s \sum_{s'=1} K_{ss'} \, n_{s'}$$

where the first term corresponds to the rate formation of s-clusters, obtained from the coalescence of s' and s" clusters (s' + s" = s), and the second to the rate at which s-clusters are lost due to the coalescence of an s-cluster with another s' cluster. This equation seems to be reasonably valid for infinite mobility since every cluster can coalesce with another no matter how far apart they are.

An analysis of the solution of this equation shows that the critical exponents strongly depend on the coagulation rate $K_{ss'}$[38].

Another kinetic model originally suggested by Manneville and de Seze[39] considers a lattice system in which sites can be occupied by two-functional or four-functional units. The bond formation is obtained by random motion of active centers. This can be considered the kinetic version of a static model[40][41] which was introduced to study polymer gelation. This model differs from the kinetic one only with respect to bond formation which is completely random. The static model exhibits random-percolation exponents, except for special values of the paramers for which a crossover to self-avoiding walk is found.

The kinetic model of Manneville and de Seze has been improved and deeply studied by Monte Carlo methods.[42] The conclusion of this analysis is that the ratio of the amplitudes of the second-momentum distribution above or below p_c, is different from what is found in random percolation or in classic theories. This suggests that this kinetic model belongs to a new class of universality. The deviation from the universality class of random percolation cannot be attributed to the mixture of two and tetra-functional units, as demonstrated in the static model. Therefore it is more plausible to attribute this change to the kinetic aspect of the model. Also in other models of cluster growth, although non-pertinent to gelation, different kinetic models gave different critical exponents[43]. All these results seem to indicate that critical exponents seem to be rather sensitive to the details in the kinetic assumptions.

9. - Conclusions

The main features of SOL-GEL transition is connectivity. A good starting point seems to be the random-percolation model for a system without solvent and its generalization, the site-correlated random-bond percolation model, to describe also solvent effects. A better founded theory for viscosity and elasticity is needed. Experimental data analysis seems to indicate better agreement with percolation models rather than with classical theories. However more accurate experiments in the critical region and new experiments to investigate solvent effects are needed.

The kinetics seems to play an important role which must be taken into account for further theoretical developments.

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