

6

Gelation

6.1 Introduction

A **gel** is a material composed of subunits that are able to bond with each other in such a way that one obtains a network of macroscopic dimensions, in which all the subunits are connected by bonds. If one starts out with isolated subunits, and successively adds bonds, one goes from a liquid—a **sol**—to a material with a non-zero shear modulus—a **gel**. A gel has the mechanical properties characteristic of a solid, even though it is structurally disordered and indeed may contain a high volume fraction of liquid solvent. If the gel consists of linear segments joined together at cross-link points, and the linear sections are flexible and long enough to be considered as random walks, the mechanical properties of the gel may be described by the theory of rubber elasticity described in the last chapter. Gels may also go through a glass transition: gels with a high density of short rigid segments are likely to be glassy.

Within this broad framework there are many different types of gel, with different classes of subunit, and with different types of bonding between them. For example, the subunits may be multi-functional monomers, which are connected together by covalent bonds to form a three-dimensional network. An example would be an epoxy resin. Alternatively, the subunits may themselves be linear polymers, which are connected together by covalent cross-links to form a rubber. Linear polymers may be connected by physical, rather than chemical, bonds, giving a **thermoreversible** gel such as gelatin. The subunits themselves may be colloidal aggregates of many molecules, which then are linked together by physical interactions.

Is there anything that unites these very disparate classes of materials? One common theme is that they all undergo a transition from the sol state to a gel by a process of increasing the number of bonds between subunits until there is a macroscopic network of subunits which are all connected together. This transition is known as the **gelation** transition or the **sol-gel** transition. As we shall see, it has some similarities with the thermally driven phase transitions that form such a recurring theme throughout this book. Steered by that analogy, one may ask if there are universal features of the sol-gel transition that are common throughout this wide variety of systems. We shall see that there is now reason to suppose that there is some degree of universality, though opinion is still divided as to how useful this is. Nonetheless, the sol-gel transition provides a valuable framework for us to discuss this important class of soft matter.

Thus we proceed to ask two questions, one specific, and one general.

1. What is the nature of the bonds between the subunits and how does a given system form a gel?

6.1	Introduction	95
6.2	Classes of gel	96
6.3	The theory of gelation	97

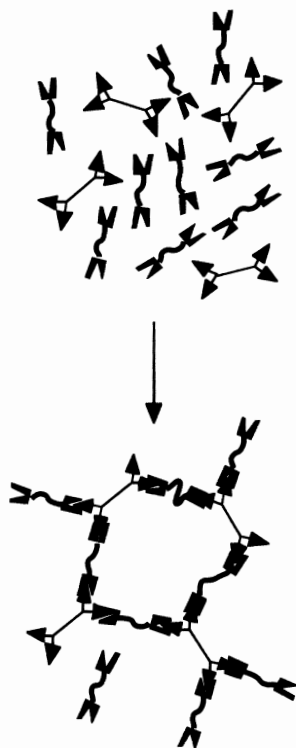


Fig. 6.1 Schematic of a thermosetting gel. The system consists of a mixture of short chains with reactive groups at each end, and cross-linker molecules, each with four functional groups capable of reacting with the ends of the chains. As the reaction proceeds the chains are linked together by the cross-linker to form an infinite network.

We will see that although there are some common themes there are a variety of detailed mechanisms for making a gel.

2. What are the general features of this kind of transition between a liquid (a sol) and a solid (a gel)?

This can be thought of as a sharp transition, with strong analogies to phase transitions driven by temperature changes, and as for the case of phase transitions we find elements of universality connecting the behaviour of apparently different systems.

6.2 Classes of gel

We can divide gels into two classes, depending on the nature of the bonds that link the subunits.

Chemical gels—the bonds linking the subunits are covalent chemical bonds.

Physical gels—the bonds linking the subunits are physical interactions.

Physical gels are sometimes also known as thermoreversible gels, as usually the physical interactions are of the form that are disrupted by increasing the temperature. One can melt a jelly, but not a cured epoxy resin.

6.2.1 Chemical gels

To make a chemical gel, one needs multi-functional units that can be linked by chemical bonds to make a three-dimensional network. The idea is illustrated in Fig. 6.1. Subunits that are difunctional cannot make a network; they can only make a collection of linear polymers. Among examples of systems which form this kind of chemical gel are:

- **Thermosetting resins.** Materials such as epoxy resins are formed from a resin, which is a short polymer with reactive groups on both ends, and a hardener, which consists of a multi-functional molecule that can react with up to four resin end groups. When the resin and hardener are mixed the resin molecules are linked together to form a three-dimensional network. The increase in effective relative molecular mass of the growing clusters generally leads to a transition into the glassy state, so when cured epoxy resins are hard, stiff materials.
- **Sol-gel glasses.** Certain organic derivatives of silicon oxide and metal oxides are soluble in organic solvents, and in the presence of water will link together following the hydrolysis of their organic groups. In this way gels which are chemically similar to inorganic glasses may be formed by solution processing rather than by melting silica and metal oxides at high temperatures.

In both of these cases, we are forming a gel by starting out with small units which polymerise. We can also begin with long, linear polymers which we subsequently cross-link. This gives us another category of chemical gels:

- **Vulcanised rubbers.** The process on which the rubber industry was founded relied on cross-linking natural rubber—the linear polymer polyisoprene—using sulphur to yield a tough, elastic material. Modern

technology uses different cross-linking agents, but the principle is the same. The basic idea is sketched in Fig. 6.2. One starts with an entangled melt of linear polymers; adjacent segments are randomly linked. As the density of cross-links increases we expect the modulus of the material to increase according to eqn 5.29. At very high cross-link densities the material becomes glassy.

6.2.2 Physical gels

In a physical gel, units are joined together by bonds which are physical in character, not chemical. These bonds can generally be broken by heating the system, so this type of gel is known as thermoreversible. Mechanisms by which such reversible cross-links can be formed include the following:

- **Microcrystalline regions.** In a number of polymer solutions, in regions where polymer chains meet they may begin to form small crystalline regions linking more than one chain (see Fig. 6.3). These form cross-links, but if the system is heated above the melting point of the crystallites then the cross-links will be broken, to reform again if the solution is cooled down again. The most familiar everyday example is table jelly, which is made from gelatin. Gelatin is the product of chemically degrading collagen, the group of proteins which form the major structural components of connective tissue. In its native state, the protein chains of collagen form a triple helix structure (see Fig. 6.4). When a solution of gelatin is cooled, chains come together to form little regions of triple helix; these form junctions effectively cross-linking the chains together. Because this process amounts effectively to forming small crystalline regions, there is a fairly well-defined melting point.
- **Microphase separation.** As we shall see in Chapter 8, a polymer in which two chemically different polymer segments are linked together covalently—a **block copolymer**—can **microphase separate**. This is illustrated in Fig. 6.5; here we envisage triblock copolymers, in which a long section of a rubbery polymer such as polybutadiene has attached at either end shorter blocks of a glassy polymer such as polystyrene. The polystyrene blocks will microphase separate into small spherical domains; because the polystyrene is glassy at room temperature the polystyrene ends will be firmly anchored into the domains, which will thus act as cross-link points for the longer, rubbery polybutadiene chains. However, if the material is heated above the glass transition temperature the polystyrene ends are no longer firmly held within the domains and the material becomes a melt. Such materials are known commercially as **thermoplastic elastomers**, and are used for applications such as shoe soles.

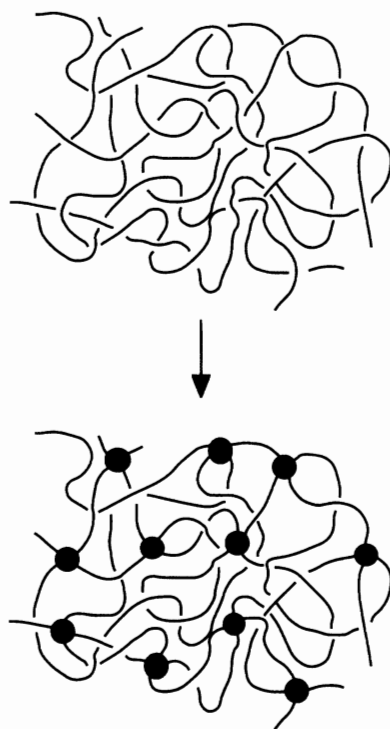


Fig. 6.2 Schematic of a vulcanisation reaction. The system consists of a mixture of long chains. Initially, the chains are entangled but not covalently linked. The reaction proceeds by chemically linking adjacent chains, leading to the formation of an infinite network.

6.3 The theory of gelation

6.3.1 The percolation model

A curious feature of gelation is the fact that as we create more bonds in a continuous way, the macroscopic properties of the gel change

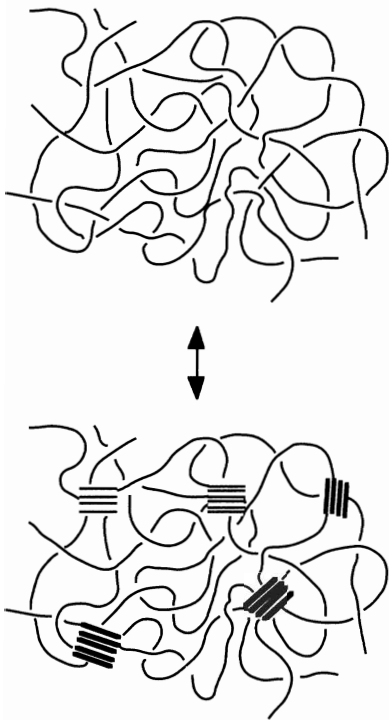


Fig. 6.3 Thermoreversible gelation by the formation of microcrystals. At low temperatures (bottom) adjacent chains form small crystalline regions which act as cross-links. Above the melting temperature, the cross-links disappear (top).



Fig. 6.4 Collagen molecules in their native conformation. Each chain is a left-handed helix; the three chains assemble to form a right-handed superhelix.

discontinuously: when a certain fraction of bonds has been made, the sample changes abruptly from a liquid- to a solid-like material. We can make a simple model that exhibits this kind of behaviour. Although the microscopic details of gelation in the many different systems that exhibit the phenomenon may be different, we might hope that there are some generic features of the transition that will be captured in a simple model. This model is the **percolation model**. It is illustrated in Fig. 6.6. We imagine an array of points which can be joined by bonds. As more bonds are added at random, clusters of points are formed, until at some stage we form a cluster that spans the entire lattice. This marks the gelation point

Among the questions we need to ask are:

- what is the fraction of bonds that need to be made in order to obtain an infinite cluster;
- how does the average cluster size vary with the fraction of bonds;
- when an infinite lattice is formed, what proportion of bonds belong to the infinite lattice as a function of fraction of bonds; and
- if the bonds represented a physical network, how would the elasticity of the network depend on the fraction of bonds?

It turns out that these questions cannot be answered by analytical methods for the percolation problem on a simple lattice as illustrated in Fig. 6.6. The problem is, however, extremely well suited to computer simulation and many results have been thus obtained. Before considering these general results, let us consider another special model which can be solved analytically.

6.3.2 The classical theory of gelation—the Flory–Stockmayer model

In this model, we consider connecting points on a **Cayley tree**. Thus we start with one point, which can connect to z other points. Each of these other points can in turn connect with z further points, and so on to infinity. This is illustrated in Fig. 6.7.

Suppose that the probability that a bond is made is f (i.e. the fraction of reacted bonds is f and we assume that each bond is independent of every other bond). Each monomer in the n th generation will be linked to $f(z-1)$ monomers in the $(n+1)$ th generation. Thus if we count the number of bonds in the cluster out to the n th generation, N , we find

$$N \sim f(z-1)^n. \quad (6.1)$$

So as the number of generations n goes to infinity we find two types of behaviour, depending on whether f is greater than or less than a critical value f_c :

$$\text{if } f < f_c \quad N \rightarrow 0 \text{ as } n \rightarrow \infty \quad (6.2)$$

$$\text{if } f > f_c \quad N \rightarrow \infty \text{ as } n \rightarrow \infty \quad (6.3)$$

where f_c defines the **percolation threshold**, and is given by

$$f_c = \frac{1}{z-1}. \quad (6.4)$$

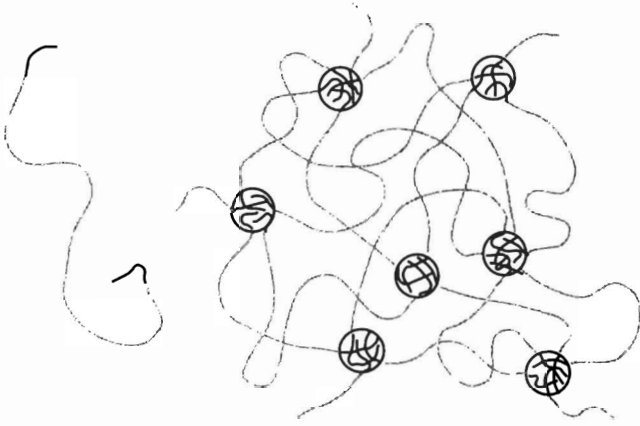


Fig. 6.5 A triblock copolymer (left) can form a thermoplastic elastomer. The end blocks microphase separate to form small, spherical domains. When these domains are glassy they act as cross-links for the rubbery centre blocks; the rubber can be returned to the melt state by heating above the glass transition of the end blocks.

Thus for $f < f_c$, below the percolation threshold, we have a solution of finite clusters—a sol. As we approach the percolation threshold, the mean size of the clusters diverges, and properties like the viscosity, which depend on the mean cluster size, also diverge.

For $f > f_c$, above the percolation threshold, we have an infinite cluster—a gel. This has a finite shear modulus.

It is important to recognise that above the percolation threshold, even though there is an infinite cluster, not all bonds are part of it. The fraction of bonds that are part of the infinite cluster is called the **gel fraction** and may be calculated in the following way.

We refer to the diagram in Fig. 6.8. Suppose that the probability that a certain site is connected to infinity by a continuous path of bonds is P , and the probability that a site is not connected to infinity by **one specified branch** is Q .

Now if we consider a neighbour to the site, we see that the probability that *none* of the neighbour's sub-branches connect to infinity is Q^{z-1} . Thus the probability that a site is connected to a neighbour, but not connected via that neighbour to infinity, is fQ^{z-1} .

This allows us to write a recursive relation for Q . If a site is not connected to infinity by a specified branch this is because *either* the site is not connected to the neighbour in that branch, *or* the site is connected to that neighbour, but that neighbour is not connected to infinity. Thus we can write

$$Q = 1 - f + fQ^{z-1}. \quad (6.5)$$

Taking the simplest case of $z=3$ this gives us a quadratic for Q with the solutions

$$Q = 1 \quad \text{or} \quad \frac{1-f}{f}. \quad (6.6)$$

Now we can find P , the fraction of bonds connected to infinity.

Q^z is the probability that a site is not connected to infinity, and fQ^z is the probability that a site is connected to a specified neighbour, but not connected to infinity. This is equal to $f - P$, the fraction of bonds that are reacted, but which do not form part of the infinite cluster.

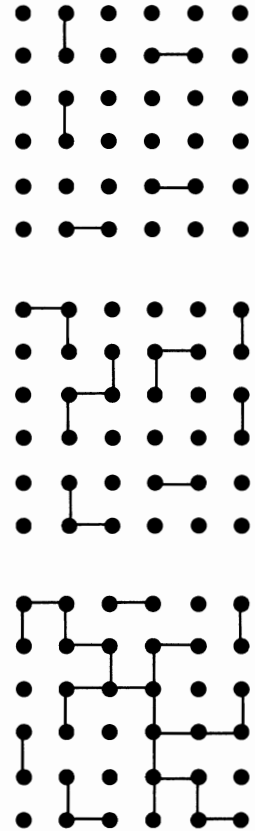


Fig. 6.6 The percolation model. We start with array of points, to which bonds are added at random (top). As more bonds are added, clusters of points are formed (middle), which ultimately join to form a cluster which spans the entire system (bottom).

Thus $f - P = fQ^z$. Once again taking the special case of $z = 3$ and using eqn 6.5 we find

$$\frac{P}{f} = 1 - \left(\frac{1-f}{f}\right)^3 \quad \text{for } f > f_c \quad (6.7)$$

or

$$\frac{P}{f} = 0 \quad \text{for } f < f_c. \quad (6.8)$$

The quantity P/f is the fraction of reacted bonds that form part of the infinite network—the **gel fraction**.

We plot this function in Fig. 6.9. The gel fraction abruptly rises from zero at the gel point; in fact we can see that close to the gel point the gel fraction can be expanded as a power law function of the distance away from the gel point. To leading order this gives

$$\frac{P}{f} = 3(f - f_c) + O(f - f_c)^2. \quad (6.9)$$

This kind of power law divergence of quantities close to a critical point is characteristic of phase transitions, emphasising the relationship between gelation and a thermal phase transition.

6.3.3 Non-classical exponents in the percolation model

In the study of thermal phase transitions, one generally finds that one can use mean field models to predict phase transitions, and that these models predict that certain quantities diverge near the transition according to a power law, but that the predicted exponents in the power law are incorrect (Chaikin and Lubensky 1995). These shortcomings are due to the neglect of fluctuations in mean field theories.

The same thing is true for percolation. The mean field model—in this case the classical Flory–Stockmayer theory described above—predicts the existence of the critical point, and predicts power law divergences near the critical point. For example, the gel fraction can be written $P/f \sim (f - f_c)^\beta$ where the exponent $\beta = 1$ in the Flory–Stockmayer theory. Monte Carlo studies of bond percolation in three dimensions give, by contrast, a value of $\beta = 0.41$. The classical theory is incorrect in detail because it neglects the possibility that **closed loops** can be formed. In general, one can expect that close to the gelation point there will be similar discrepancies between any predictions of the classical theory and the results of experiment or computer simulation.

6.3.4 The elasticity of gels

If we reduce the number of bonds towards the critical fraction f_c , we would expect the modulus of the gel (either the shear modulus or the Young modulus)

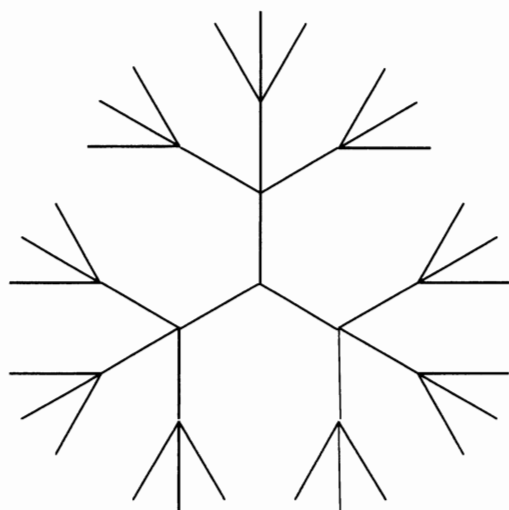


Fig. 6.7 Three generations of a Cayley tree.

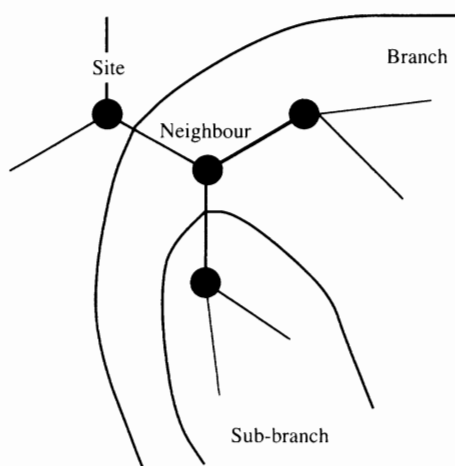


Fig. 6.8 Definitions of branches and neighbours on a Cayley tree.

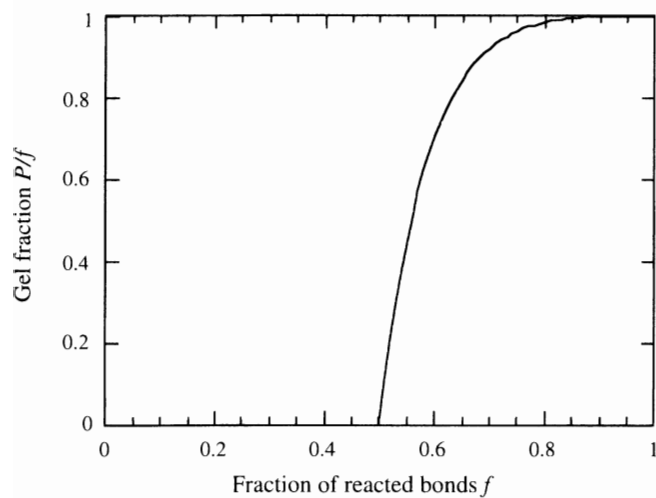


Fig. 6.9 The gel fraction in the classical model of gelation for a coordination number $z = 3$, as given by eqns 6.7 and 6.8.

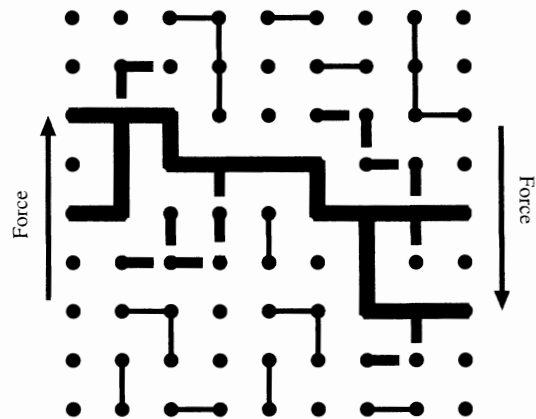


Fig. 6.10 The effect of dangling ends on the shear modulus of a gel near the gel point. The bonds shown with dashed lines are part of the infinite network, but do not contribute to the elastic modulus.

to go to zero. At first, one might imagine that it would go to zero in the same way as the gel fraction. However, further thought suggests that this cannot be the case, because of the effect of **dangling ends**. This is illustrated in Fig. 6.10: here the bonds that are shown with dashed lines are part of the infinite network, but because they are only connected to the network by one end they cannot contribute to the transfer of stress across the sample.

There is a possible analogy here with the conduction of electricity through a random network. Here one imagines making a circuit by connecting randomly selected adjacent points on a lattice with resistors. Resistors that are not in a continuous pathway from one contact to the other do not contribute to the conductance of the network Σ . Both numerical studies and experiments show that the conductance goes to zero at the gelation point with a power law with an exponent μ :

$$\Sigma \sim (f - f_c)^\mu. \quad (6.10)$$

For the 3d bond percolation model the exponent $\mu \approx 2.0$, while for the Flory-type models one finds the larger value of $\mu = 3$.

Experiments on the modulus of networks just above the gel point do seem to show power law behaviour, though the exponent is not always in agreement with that predicted for the conductance of random networks. It is possible that the correspondence between the modulus of a network and the conductance of a resistor network is not exact, because the bending rigidity of the bonds must be important in real gelling systems.

Further reading

Percolation theory and its applications are described in Stauffer and Aharony (1994). Both the classical theory of polymer gelation and the application of percolation theory to the polymer problem are described in de Gennes (1979).

Exercises

- (6.1) In a certain chemical cross-linking reaction involving a monomer that can react at three sites, the degree of reaction f obeys the second-order rate law

$$\frac{df}{dt} = k(1 - f)^2,$$

where the rate constant k has the value $4 \times 10^{-4} \text{ s}^{-1}$. Use the Flory–Stockmayer theory to calculate

- the time at which the gel point is reached,
- the time after which three-quarters of the monomers have been polymerised,

- the time after which three-quarters of the monomers form part of the infinite network.

- (6.2) In an experiment to test the application of the theory of percolation to gelation, the gel fraction is determined when the fractional extent of reaction is a small degree Δf larger than its value at the gel point.

- Is the value of the gel fraction at a fractional extent of reaction $\Delta f/2$ larger or smaller when predicted by percolation theory than the value predicted by Flory–Stockmayer theory?
- By what factor do the two predictions differ?