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 the subunits are connected by bonds. If one starts out with isolated subunits, ad 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 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 converted 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 thermoplastic 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 some 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?
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 a lot of universality connecting the behavior 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 thermo-reversible gels, as usually the physical interactions are of the form that are disrupted by increasing 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. 6.2. Subunits that are difunctional cannot make a network; they can only make a collection of linear polymers. Among examples of systems which let this kind of chemical gel we have:

- Thermosetting resins. Minerals such as epoxy resins are formed from a resin, which is a short polymer with reactive groups on both its ends and a hardener, which consists of a multi-functional molecule that reacts with up to four resin end groups. When the resin and hardener are mixed the resin molecules are linked together to form a functional network. The increase in effective molecular mass of the growing clusters generally leads to a transition into the glass state. So when cured epoxy resins are hard, stiff minerals.

- Sol-gel glasses. Certain organics, derivatives of silica and other oxides are soluble in organic solvents and, in the presence of water at limits together following the hydrolysis of their organic groups. In this way gels which are chemically similar to inorganic glasses can be formed by solutions 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 high molecular weight polymer and we can also begin with high molecular weight polymers which are subsequently cross-link. This gives us another category of chemical gels:

- Vulcanized rubbers. The process on which the rubber industry is founded relies on cross-linking natural rubber—the linear polyisoprene—using sulfur to yield a tough, elastic material. Made
6.5 The theory of gelation

6.5.2 Physical gels

A physical gel, unlike a solid, is a network of interacting molecules and cannot be melted to flow freely. The bonds that hold the network together are non-covalent, such as hydrogen bonding or van der Waals forces.

6.6 The theory of gelation

6.6.1 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

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Fig. 6.2 Schematic of a vitrification 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 interpenetrating network.
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 behavior. Although the microscopic details of gellation in the many different systems that exhibit this 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 good 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 can with one going on, which can connect to other points. Each of these other points can in turn connect with 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

\[
N \sim f(z-1)^n.
\]

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

\[
\begin{align*}
\text{if } f &< f_c \quad N \to 0 \text{ as } n \to \infty \\
\text{if } f &> f_c \quad N \to \infty \text{ as } n \to \infty
\end{align*}
\]

where \( f_c \) defines the percolation threshold, and is given by

\[
f_c = -\frac{1}{z-1}.
\]
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 some of the neighbour’s sub-branches connect to infinity is $Q^{-1}$. Thus the probability that a site is connected to a neighbour, but not connected via that neighbour to infinity, is $fQ^{-1}$. 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 the neighbour is not connected to infinity. Thus we can write

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

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

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

Now we can find $P$, the fraction of bonds connected to infinity. $Q^{-1}$ is the probability that a site is not connected to infinity, and $fQ^{-1}$ 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.
Thus \( f - P = \frac{1}{Q} \). Once again taking the special case of \( z = 3 \) and using eqn 6.5 we find
\[
P f = 1 - \left( \frac{1 - f}{f} \right)^3 \quad \text{for} \quad f > f_4
\]
\[
\text{or}
\]
\[
P f = 0 \quad \text{for} \quad f < f_4
\]

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
\[
P f = 3(f - f_4) + O(f - f_4)^2.
\]

This kind of power law divergence of quantities close to a critical point is characteristic of phase transitions, emphasizing 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 (Chakravorty 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 \( P f \sim (f - f_4)\beta \) 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 \( f_4 \), 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 in 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.
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 \( \Sigma \). Both numerical studies and experiments show that the conductance goes to zero at the gelation point with a power law with an exponent \( \mu \):

\[
\Sigma \sim (1 - f_c)^\mu. \tag{6.10}
\]

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 bond must be important in real gelting systems.

**Further reading**

Percolation theory and its applications are described in Stauffier 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

a) the time at which the gel point is reached,
b) the time after which three-quarters of the monomers have been polymerized.

c) 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 \( \Delta f/2 \) larger than its value at the gel point.

a) 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?
b) By what factor do the two predictions differ?