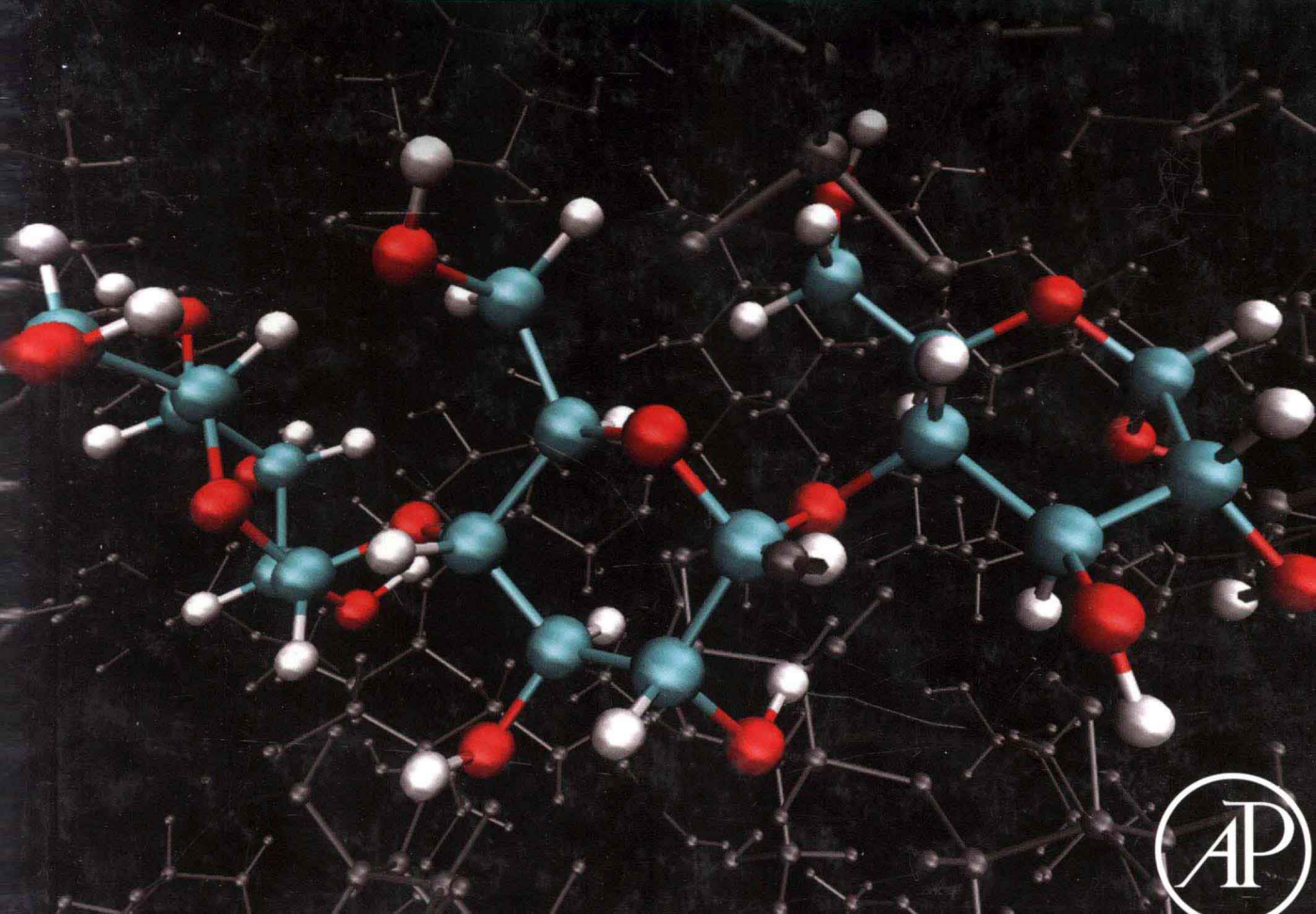
Edited by
Stefan Kasapis • Ian T. Norton • Johan B. Ubbink

Modern Biopolymer Science

Bridging the Divide between Fundamental Treatise and Industrial Application



MODERN BIOPOLYMER SCIENCE

BRIDGING THE DIVIDE BETWEEN FUNDAMENTAL TREATISE AND INDUSTRIAL APPLICATION

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Preface

It has been a while since a book was put together to address the issues of the physics and chemistry of biopolymers in industrial formulations, including concise treatments of the relation between biopolymer functionality and their conformation, structure, and interactions. In these intervening years, some materials and concepts came to prominence while other ones have changed in their appeal or application. As ever, the industrialist is faced with the challenge of innovation in an increasingly competitive market in terms of ingredient cost, product added-value, expectations of a healthy life-style, improved sensory impact, controlled delivery of bioactive compounds and, last but not least, product stability. Proteins, polysaccharides and their co-solutes remain the basic tools of achieving the required properties in product formulations, and much has been said about the apparent properties of these ingredients in relation to their practical use. There is also an ever increasing literature on the physicochemical behaviour of well-characterised biopolymer systems based on the molecular physics of glassy materials, the fundamentals of gelation, and component interactions in the bulk and at interfaces. It appears, however, that a gap has emerged between the recent advances in fundamental knowledge and the direct application to product situations with a growing need for scientific input.

The above statement does not detract from the pioneering work of the forefathers in the field who developed the origins of biopolymer science. For example, there is no question that the pioneering work on conformational transitions and gelation, the idea of phase separation into water in emulsions, the development of physicochemical understanding that lead to the concept of fluid gels and the application of the glass transition temperature to dehydrated and partially frozen biomaterials has resulted not only in academic progress but in several healthy and novel products in the market place. Thus the first phase of the scientific quest for developing comprehensive knowledge at both the theoretical and applied levels of functional properties in basic preparations and systems has largely been accomplished. It is clear, though, that the future lies in the utilization of this understanding in both established and novel foodstuffs, and non-food materials (e.g. pharmaceuticals) with their multifaceted challenges. A clear pathway for processing, preservation and innovation is developing which is particularly important if progress is to be made in the preparation of indulgent yet healthy foods which are stable, for example, in distribution and storage. This requires a multi-scale engineering approach in which material properties and microstructure, hence the product performance are designed by careful selection of ingredients and processes. Examples of this can be found in the pioneering work on fat replacement and the reliance on the phenomenon of glass transition to rationalise the structural stability and mouthfeel of a complex embodiment.

Within this context of matching science to application, one feels compelled to note that a dividing line has emerged, which is quite rigorous, with researchers in the structure-function relationships of biopolymers opting to address issues largely in either high or low-solid systems. This divide is becoming more and more

pronounced, as scientists working in the high-solid regime are increasingly inspired by the apparently "universal" molecular physics of glassy materials, which may or may not consider much of the chemical detail at the vicinity of the glass transition temperature. By comparison, their colleagues working on low-solid systems are shifting their focus from the relatively universal structure-function relationships of biopolymers in solution to the much more specific ones involving multi-scale assembly, complexation and molecular interactions. Sharing the expertise of the two camps under the unified framework of the materials science approach is a prerequisite to ensuring fully "functional solutions" to contemporary needs, spanning the full range of relevant time-, length- and concentration scales. This effort may prove to be the beginning of a modernized biopolymer science that, one the one hand, utilizes and further develops fundamental insights from molecular physics and the advanced synthetic polymer research as a source of inspiration for contemporary bio-related applications. On the other hand, such modernized science should be able to forward novel concepts dealing with the specific and often intricate problems of biopolymer science, such as the strong tendency for macromolecular hydrogen bonding, thus serving as an inspiration for related polymer advances and industrial applications. Sincere thanks are due to all our friends and colleagues whose outstanding contributions within their specialized areas made this a very worthwhile undertaking.

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Contents

CHAPTER

1

Biopolymer Network Assembly: Measurement and Theory

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A number of biopolymer systems can self-assemble to form networks and gels and the assembly can occur by a variety of mechanisms. In this chapter we consider the nature of biopolymer gels and networks, the kinetics of assembly, and their characterization by rheological methods. The necessary theory to explain, for example, the complexities of gelation kinetics is then described in some detail. Before reaching this, we discuss the nature of network assembly, and the character of gels and their gelation.

1.1 BIOPOLYMER NETWORKS AND GELS

1.1.1 Gels Versus Thickeners

1.1.1.1 What is a Polymer Network?

Polymer networks are molecular-based systems, whose network structure depends upon covalent or non-covalent interactions between macromolecules. The interactions can be simple covalent cross-links, or more complex junction zone or particulate-type interactions. Figure 1.1 illustrates different types of polymer network. Solvent swollen polymer networks are commonly known as gels – un-swollen networks are important for synthetic polymer systems, but are less relevant for biopolymers. Here, where the solvent is water or electrolyte, we can also introduce the term 'hydrogel'.

1.1.1.2 What is a Gel?

We have already defined a gel above as a swollen polymer network, but unfortunately, one of the major issues in chapters such as the present one is that the term 'gel' means very different things to different audiences. In this respect, the widely cited 1926 definition by Dorothy Jordan Lloyd, that 'the colloidal condition, the gel, is one which is easier to recognize than to define' (Jordan Lloyd, 1926) is quite unhelpful, since it implies that a gel is whatever the observer thinks it is. Consequently we commonly see such products described as shower gels and pain release or topical gels.

Neither of these classes of systems follows a rheological definition such as that of the late John Ferry, in his classic monograph (Ferry, 1980). He suggests that a gel is a swollen polymeric system showing no steady-state flow; in other words if subjected to simple steady shear deformation it will fracture or rupture. Clearly neither shower nor topical gels follows this rule;

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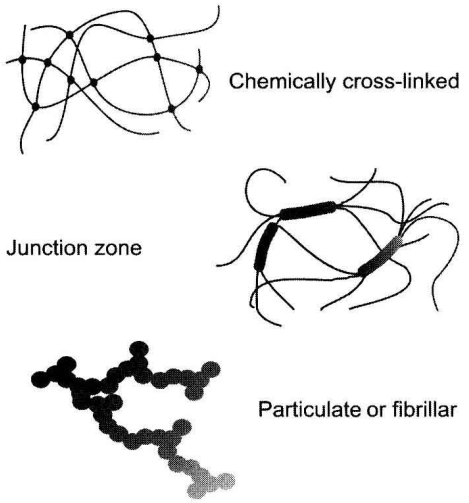

FIGURE 1.1 These diagrams illustrate three different types of polymer network; note that the three figures are not necessarily to scale.

indeed if they did, they would not be useful as products. In fact, commercial shower gels, for example, are simply highly viscous fluids formed by the entanglement of (often rod-like) micelles. For more rigorous definitions, at this stage it is necessary to introduce some common terminology.

Most modern rheological experiments on gelation (see below) employ oscillatory shear. In the simplest form of this, a small sinusoidal strain wave of frequency ω (typically 10^{-3}–10 s^{-1}) is applied to the top surface of a gelling system (most likely constrained between parallel metal discs) and the resultant stress transmitted through the sample is measured. In general the stress and strain waves differ in both phase and amplitude, but using phase resolution, it is easy to extract the in-phase and 90° out-of-phase components. Then G′ is the storage modulus given as the ratio of in-phase stress divided by strain, and G″ is the loss modulus, the ratio of 90° out-of-phase stress to strain. There are other relationships between these and common experimentally determined parameters, as we describe later, but for now we are interested only in the storage – sometimes called elastic component – of the modulus, G′. For a perfect, so-called Hookean elastic material, such as a steel rod, G′ is effectively independent of the oscillatory frequency. The constancy of G′ with respect to frequency is then a useful definition of a solid.

One rheological definition of a gel is therefore a system that shows 'a plateau in the real part of the complex modulus' – G′ – 'extending over an appreciable window of frequencies ... they are ... viscoelastic solids' (Burchard and Ross-Murphy, 1990). A slightly later definition accepts this, but extends it and the Ferry definition by identifying a gel as a soft, solid or solid-like material, which consists of two or more components, one of which is a liquid, present in substantial quantity (Almdal et al., 1993). They therefore follow Ferry in accepting substantially swollen polymer networks as gels. However, according to them, a gel must also show a flat mechanical spectrum in an oscillatory shear experiment. In other words it should show a value of G′ which exhibits a pronounced plateau extending to times of the order of seconds, and a G″ which is considerably smaller than the storage modulus in this region.

1.1.1.3 'Viscosifiers'

One of the problems in this area follows directly from the overuse of the term gel – as we outlined above, many viscous fluids are also described as gels or hydrogels. These include biopolymer solutions, whose properties are determined all but exclusively by entanglements of long chains, in this area typically represented by solutions of the galactomannan guar. These are analogous to solutions of common synthetic polymers in organic solvents, where entanglements involve reptation of chains (Doi and Edwards, 1986). Rheologically there are also a number of so-called structured liquids – which can suspend particles and appear

solid-like – typically formed from liquid crystalline polymers or micellar solutions – and usefully exemplified in the present context by ordered solutions of the microbial polysaccharide xanthan (Richardson and Ross-Murphy, 1987b). To confuse matters, these have been referred to, in the past, including by one of the present authors as 'weak gels' (Ross-Murphy and Shatwell, 1993). We now reject this term totally, both because of its anthropomorphic connotation, and for its lack of precision – since they can show steady-state flow – in terms of the Ferry definition above.

1.1.1.4 Viscoelastic Solids vs. Viscoelastic Liquids

What then is the main difference between solids and liquids? It is the existence of an equilibrium modulus, i.e. a finite value of G′ even as the time of measurement becomes very long (or the oscillatory frequency tends to zero), usually referred to simply as the equilibrium shear modulus G. This means that a gel has (at least one) infinite relaxation time. Of course such a definition is partly philosophical, since given infinite time, all systems show flow, and in any case, most biopolymer gels will tend to degrade, not least by microbial action. However, this remains an important distinction, and in subsequent pages we regard biopolymer networks and gels as viscoelastic solids, and non-gelled systems, included pre-gelled solutions, 'sols', as viscoelastic liquids.

1.1.2 Brief History of Gels

1.1.2.1 Flory Types 1–4

Historically the term gel follows from the Latin gelatus 'frozen, immobile', and gelatin, produced by partial hydrolysis of collagen from, e.g. pigs, cattle or fish was probably recognized by early man. Gelatin has certainly been used in photography for almost 150 years, although this is, of course, a shrinking market.

In 1974, Flory (Flory, 1974) proposed a classification of gels based on the following:

1. Well-ordered lamellar structure, including gel mesophases.
2. Covalent polymeric networks; completely disordered.
3. Polymer networks formed through physical aggregation, predominantly disordered, but with regions of local order.
4. Particular, disordered structures.

In the present chapter, although we will not discuss specific systems in much depth, type 3 gels are represented by 'cold set' gelatins, and type 4 gels are represented by denatured protein systems. Type 2 systems are archetypal polymer gels. These are made up, at least formally, by cross-linking simpler linear polymers into networks, and their mechanical properties, such as elasticity, reflect this macroscopic structure.

1.1.2.2 Structural Implications

The structural implications of the above should be clear – gels will be formed whenever a super-molecular structure is formed, and Figure 1.1 illustrates the underlying organization of type 2, 3 and 4 gels. Of course this is highly idealized; for example if the solvent is 'poor', gel collapse is seen. Examples of each of these classes include the rubber-like arterial protein elastin – type 2; many of the gels formed from marine-sourced polysaccharides such as the carrageenans and alginates, as well as gelatin, type 3; and the globular protein gels formed by heating and/or changing pH, without substantial unfolding, type 4.

Of course, Figure 1.1 is highly idealized and the nature of network strands can vary substantially. For example, for the polysaccharide gels, such as the carrageenans, the classic Rees model of partial double helix formation (Morris et al., 1980) has been challenged by both small-angle X-ray scattering (SAXS) and atomic force microscopy (AFM)

measurements, and it now seems likely that aggregation of junction zones and intertwining of pre-formed fibrils are additional contributory factors. This is certainly an on-going controversy, but one outside the remit of this chapter, except for its implications for the kinetic processes occurring during gelation. There are similar variations for protein gels too. When heated close to the isoelectric point, a coarse and random coagulate network is commonly formed but heating many globular proteins above their unfolding temperatures under acid conditions – say at pH 2 – results in fibrillar structures (Stading et al., 1992) that, at least at the nano-length scale, resemble the amyloid structures seen in a number of critical diseases such as Alzheimer's (Gosal, 2002; Gosal et al., 2002; Dobson, 2003). This is now a very active area of research, but the subject of a separate chapter in this volume (Hughes and Dunstan, 2009).

1.2 RHEOLOGICAL CHARACTERIZATION OF BIOPOLYMER GELS

1.2.1 Traditional Methods for Gel Characterization

A number of more traditional techniques have been used for gel measurements. They often have a major advantage in their low cost, compared to commercial apparatus. On the debit side, the actual strain deformation is sometimes unknown or, at best, requires calibration. Nowadays these approaches are less commonly employed, as almost all labs possess at least one oscillating rheometer, but they still have some advantages – not least from the financial viewpoint.

1.2.1.1 Falling Ball

This is one of the simplest and cheapest methods but, given a few precautions, it can still prove useful. In its simplest form, a magnet is used to raise a small metal sphere within a tube containing gelling material, and then the time taken to fall a fixed distance is registered (Richardson and Ross-Murphy, 1981). Clearly as gelation proceeds from the sol state, the rate of fall decreases, and eventually the sphere does not move any more. For low modulus systems there are potential problems since the sphere may locally rupture the gel and cut a channel through it – so-called 'tunneling' – and in this limit the method is more akin to a large deformation or failure method. The converse method of monitoring the fall of a sphere above a melting gel (or a series of such samples at different concentrations) is very commonly used to determine 'melting temperatures' (Eldridge and Ferry, 1954; Takahashi, 1972), but again care must be taken to ensure that true melting is involved rather than localized pre-melt tunneling.

1.2.1.2 Oscillatory Microsphere

The microsphere rheometer is just the oscillatory analogue of a falling ball system. A small magnetic sphere is placed into the sample and using external AC and DC coils, the sphere can be positioned and made to oscillate with the frequency of the AC supply. The maximum deformation can be observed with a traveling microscope, or alternatively tracked, for example, using a position-sensitive detector array. A number of different designs have been published and used for measurements on systems including agarose and gelatin gels, and mucous glycoproteins (King, 1979; Adam et al., 1984). The major limitation is that the measurement is very localized, so that again for some systems local rupture and tunneling can occur and then the modulus determined may not be representative of the whole system.

1.2.1.3 U-tube Rheometer

In this very simple assembly, originally designed by Ward and Saunders in the early 1950s for work on gelatin, the gel is allowed to

set in a simple U-tube manometer, one arm of which is attached to an air line of known pressure, the other free to the air. Both may be observed with a traveling microscope. The air pressure exerts a compression stress in the sample (stress and pressure both have units of force/area), and the deformation of the sample can be measured from the differential heights of the manometer arms. The static (equilibrium Young's modulus) can be calculated directly using the analogue of Poiseuille's equation for capillary flow (Arenaz and Lozano, 1998).

As well as cheapness, this apparatus has the advantage that it becomes more sensitive for low modulus systems, since the deformation observed will be larger. However, in view of this, great care must be taken that the deformation induced is still in the linear region. The method has recently been extended for use with gels which synerese, by roughening the inner glass surfaces and by using an oscillatory set up (Arenaz et al., 1998; Xu and Raphaelides, 2005).

1.2.2 Modern Experimental Methods Employing Oscillatory Shear

Nowadays the vast majority of physical measurements on gels are made using oscillatory shear rheometry (Ferry, 1980; Ross-Murphy, 1994; Kavanagh and Ross-Murphy, 1998). This is because rheometers are far cheaper and 'user friendly' than used to be the case. However, by the same token, some published data are poor and, just as seriously, the degree of understanding does not always appear to have kept pace with the rate of data collection. One of the major objectives of succeeding sections is to try to modify this situation.

The essential features of a typical rheometer for studying biopolymer systems consists of a vertically mounted motor (which can drive either steadily in one direction or can oscillate). In a controlled stress machine, this is usually attached to the upper fixture. A stress is produced, for example by applying a computer-generated voltage to a DC motor, and the strain induced in the sample can be measured using an optical encoder or radial position transducers attached to the driven member. In a controlled strain instrument, a position-controlled motor, which can be driven from above or below, is attached to one fixture, and opposed to this is a transducer housing with torque and in some cases, normal force transducers. Figure 1.2 represents a typical controlled stress instrument. The sample geometry can be changed from, e.g. Couette, to cone/plate and disc/plate, and the sample temperature controlled. Such a general description covers most of the commercial constant strain rate instruments (e.g. those produced under the names of TA Instruments, ARES series) and controlled stress rheometers (e.g. Malvern Bohlin, TA Instruments Carrimed, Rheologica, Anton Paar). In recent years the latter have begun to dominate the market, since they are intrinsically cheaper to construct, and they can provide good specifications at lower cost. Most claim to be usable in a servo-controlled (feedback) controlled strain mode, and are widely used in this mode. However, there are limitations here, as discussed in detail below.

Controlled stress instruments are ideal for time domain experiments, i.e. measuring creep, whereby a small fixed stress is applied to a gelled sample and the strain ('creep') is monitored over time (Higgs and Ross-Murphy, 1990). The time domain constant strain analogue of the creep experiment is stress relaxation. In this, a fixed deformation is quickly applied to the sample and then held constant. The decrease in induced stress with time is monitored. Few such measurements have been discussed for biopolymer systems and nowadays practically all modern instruments appear to be used predominantly in the oscillatory mode.

1.2.2.1 Mechanical Spectroscopy

We have already introduced the storage and loss moduli, G' and G'', but there are a number of

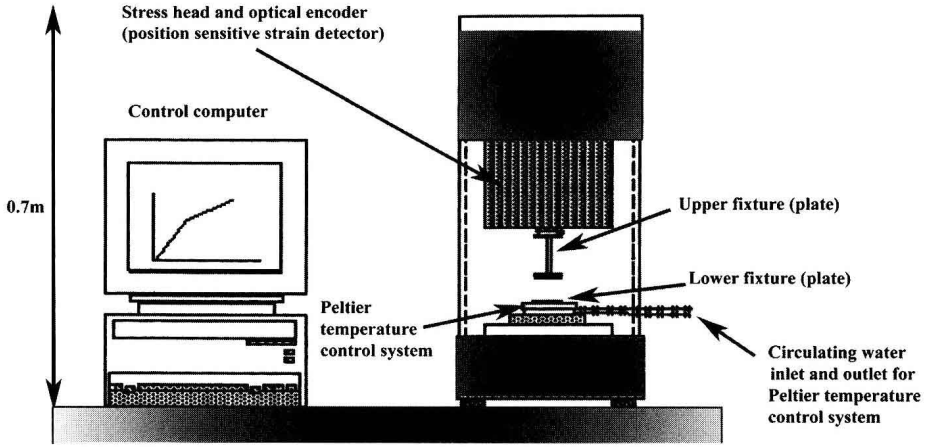

FIGURE 1.2 A typical controlled stress rheometer with parallel plate geometry.

other commonly used rheological parameters, and all are interrelated (Ferry, 1980; Ross-Murphy, 1994).

For example, G*, the complex modulus is given by:

$$G^* = \sqrt{(G')^2 + (G'')^2} \tag{1.1}$$

and the ratio:

$$\frac{G''}{G'} = \tan(\delta) \tag{1.2}$$

In the early days of oscillatory rheometry the phase angle, δ, was an experimentally observed parameter; nowadays instruments tend to hide the experimental measurables, the phase angle and the amplitude ratio, from the user.

Finally the complex viscosity, η^*, is given by:

$$\eta^* = \frac{G^*}{\omega} \tag{1.3}$$

with ω the oscillatory shear (radial) frequency; here ω is just 2π x the frequency in Hertz. Of course, oscillatory measurements can also be made in tension/compression, leading to alternative parameters, such as E′ and E″, etc. However, for biopolymer gels and networks, this is relatively uncommon, and so we do not discuss these further.

1.2.2.1.1 Controlled Strain Versus Controlled Stress We mentioned above that the majority of modern instruments are now of the controlled stress type. However most usually still generate results in the controlled strain form, that is as the modulus components, G′ and G″. Strictly speaking, since stress is applied and the strain is measured, then results should be reported as the components of complex compliance J′ and J″. However, most of the instruments circumvent this by applying a stress, measuring the strain, but in a servo- or feedback mode, so that it appears that they are indeed controlling the strain. For many applications and systems this is acceptable, but for systems very close to gelation, it is certainly not ideal. This is because there is no sure way of controlling the feedback when the system just changes from solution (sol) to gel, and yet at the same time guaranteeing that the strain remains very low. For such systems there is a further advantage in a genuine controlled strain technique, in that the mechanical driving head and the measurement

transducer are completely separate assemblies – the only link between them is the test sample and geometry.

1.2.2.1.2 Time Independent Systems Below we describe a typical experimental regime to collect the data in a form that is appropriate for an exploration of the kinetic assembly of biopolymer networks. However, since the overall outcome usually involves the conversion of a biopolymer solution (sol) to a viscoelastic solid (gel) it is useful to first understand the so-called mechanical spectra of these two systems, and their dependence on the experimental variables of oscillatory frequency, shear strain deformation (or shear stress, bearing in mind the caveats above) and temperature.

1.2.2.2 Frequency and Strain Dependence

1.2.2.2.1 Biopolymer Solutions The mechanical spectrum of a liquid has the general form illustrated in Figure 1.3. At low frequencies (note the double log scale) G″ is greater than G′ but as the oscillatory frequency increases, G′ increases more rapidly than G″ (with a slope ~ 2 in the log–log representation, compared to a slope of 1 for G″) and at some frequency there is a 'cross-over'. After this both G′ and G″ become much

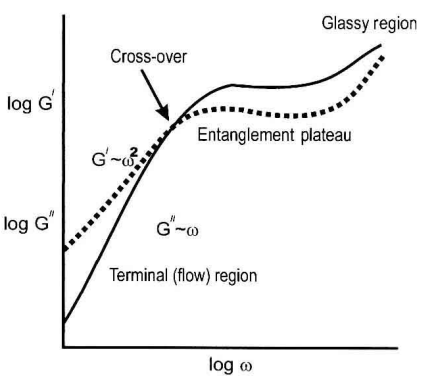

FIGURE 1.3 The mechanical spectrum of a liquid from the terminal zone to the start of the glassy region has the general form illustrated here.

less frequency-dependent – we enter the so-called rubbery plateau region.

Whether or not the cross-over region is reached in the frequency window of conventional oscillatory measurements depends upon the biopolymer concentration, relative molecular mass (MW), and chain flexibility. For example for a typical high MW viscosifier such as guar, the G″– G′ cross-over may occur for concentrations of say 2–3% w/w (Richardson and Ross-Murphy, 1987a), whereas for a more flexible and lower MW biopolymer such as gelatin above its gel melting temperature, the concentration required may be above 25% w/w, and therefore essentially outside the experimentally interesting range.

At the same time, the mechanical spectrum measured will be essentially independent of the amount of shear strain, out to say 100% 'strain units' (i.e. a strain, in terms of the geometry of deformation, of 1). Rheologists may express this by saying that the linear viscoelastic (LV) strain extends out to ca. 100%.

1.2.2.2.2 Biopolymer Gels The mechanical spectrum of a viscoelastic solid will, as we already mentioned in the discussion of the equilibrium modulus, have a finite G′, with a value usually well above (say 5–50 x) that of G″, at all frequencies, as illustrated in Figure 1.4 (Clark and Ross-Murphy, 1987; te Nijenhuis, 1997; Kavanagh et al., 1998; Kavanagh, 1998). In this respect it shows some similarities with the plateau region of the solution mentioned above – such a plateau has been referred to, somewhat imprecisely, as gel-like, for exactly this reason.

The strain-dependent behavior for biopolymer gels is more difficult to generalize, although the LV strain is rarely as great as 100% (some gelatin gels may be the exception here), and may be extremely low – say 0.1% as less. At values just greater than the LV strain, G′ and G″ may show an apparent increase with strain. This is, of course, largely an artefact of the experiment, since G′ and G″ are only defined within the LV