.

(Fourier transform mechanical spectroscopy (FTMS)

The evolution of visco-elastic properties in non-Newtonian fluids exhibiting time-dependent rheological changes is a matter of wide scientific interest, particularly so in systems undergoing gelation. The gel-point, where a three-dimensional network structure is established, may be identified rheologically by the establishment of a characteristic frequency dependence of the dynamic moduli, and an associated frequency independent loss tangent [Winter and . [Chambon, 1986

This criterion for gel-point detection, and the non-equilibrium nature of systems undergoing gelation, requires that data be obtained rapidly over a wide range of frequency, prompting the development of a frequency multi-plexing technique known as Fourier Transform Mechanical Spectroscopy, FTMS, at several frequencies *simultane-ously*,*which allows the measurement of *G* . [rather than consecutively, as in a conventional test [Holly *et al*., 1988

The technique, initially developed to measure visco-elastic properties in the curing of polymers [Malkin *et al*., 1984], has been applied to gels (In and Prud'homme, 1993) and model visco-elastic fluids [Davies and Jones, 1994]. In a variation of the technique, dynamic mechanical properties are determined using the Fourier transform of pulsed deformations [Vratsanos and Farris, .[1988

Experimental times for determining dynamic properties depend on a material's inherent time-dependent behaviour and single-point measurements must span a time period equal to that over which the sample can respond to the imposed stress or strain. This defines a *minimum* measurement time, over which a sample must be 'quasi-stable' for meaningful rheological measurement and a 'mutation number' has been proposed which expresses the relative evolution of the measured property during the experimental time [Mours and Winter, 1994].

In FTMS experiments a sample is subjected to an imposed oscillatory stress or strain. In controlled-stress FTMS, the applied stress is conveniently expressed as an applied torque (the raw experimental parameter from which stress is obtained) as:

$$C(t) = C_o \sum_{k=1,3,5...}^{n_h} \cos k\omega t \tag{2.33}$$

[Davies and Jones, 1994] where $\omega = 2\pi f$ (f in Hz) is the fundamental frequency of oscillation, C_o is the fundamental torque amplitude, and n_h is the highest harmonic in the series.

The individual components of an applied oscillatory torque of constant amplitude are illustrated in Figure 2.10, and the resulting complex torque signal, obtained from the superposition of these, is shown in Figure 2.11. This non-sinusoidal waveform for the applied torque results in an angular

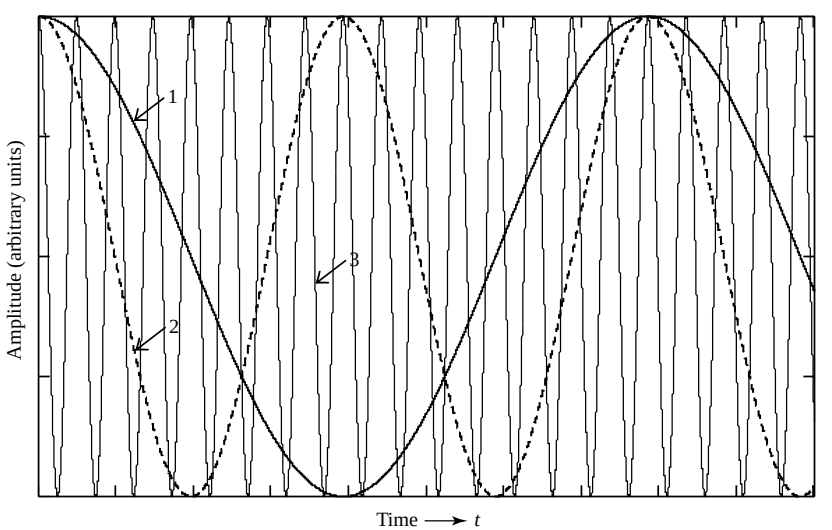

Figure 2.10 *Computer generated sinusoidal torque (or stress) signals of frequencies, 4 radian/s(curve 1), 8 radian/s(curve 2), 64 radian/s(curve 3), corresponding to integer multipliers of 1, 2 and 16, on the basis of a fundamental frequency of 4 radian/s*

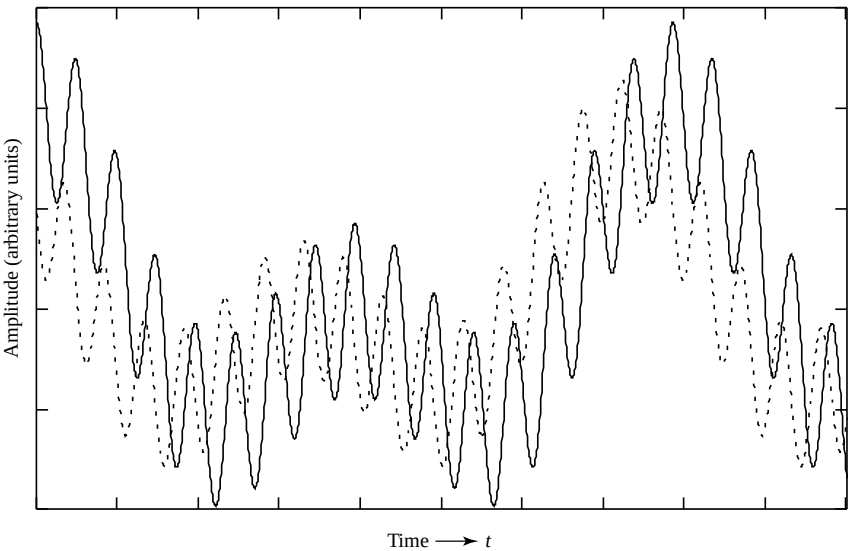

Figure 2.11 *Complex torque (stress) signal(- - -) obtained by superposition of the three waveforms shown in Figure 2.10 and a computer generated 'typical' strain response(–)*

displacement waveform to which a Fourier analysis can be applied, thereby allowing the determination of the complex visco-elastic parameters, μ^* or G^* and their components for each harmonic frequency. Basic aspects of Fourier analysis and the Fast Fourier Transform (FFT) can be found in various texts [Brigham, 1988].

The procedure for performing FTMS measurements using a controlled-stress instrument differs only slightly from conventional test procedures. The test is configured in the same manner as in a 'time sweep' but in this case the selected frequency acts as the fundamental from which further harmonics are selected, with each harmonic frequency being an integer multiple of the fundamental frequency.

An important factor in the construction of the composite waveform is the setting of the maximum strain and torque ratio for each harmonic of the fundamental. As the strain applied to the sample is the sum of the individual strains associated with each harmonic, care must be taken not to exceed the linear visco-elastic limit. For strain sensitive systems this can severely restrict the number of frequencies used.

As the value of the harmonic frequency increases, the corresponding stress amplitude decreases, resulting, eventually, in an inadequately resolved waveform. To overcome this, a torque multiplying factor is introduced which scales the fundamental torque amplitude to an adequately resolvable level. Usually an

instrument's control software allows a *maximum* strain level to be designated, which should not be exceeded by any of the harmonic strain amplitudes.

2.8 High frequency techniques

In many cases, a comprehensive characterization of the rheological properties of systems, such as concentrated colloidal dispersions, can require measurements of dynamic mechanical behaviour at frequencies outside the range of conventional, commercially available, rheometers (typically 10^{-3} Hz to 10^{2} Hz). In particular, consideration of the relative time scales of particle–fluid displacement and interfacial polarization mechanisms in such systems reveals the need for enhanced high frequency ranges (above *ca.* 10^{2} Hz).

High frequency rheometry, which usually involves wave propagation, offers some advantages over conventional techniques due to its inherent rapidity, and the (generally) small strains which are invoked. These are particularly useful features in the context of attempts to characterize the rheology of systems undergoing gelation whose non-equilibrium properties may involve pronounced mechanical weakness and strain sensitivity.

Notwithstanding the rheometrical advantages associated with these features, attempts to exploit wave propagation in monitoring processes, such as polymer curing, have achieved only partial success, due principally to the very high frequencies employed (typically 1 MHz to 10 MHz). In studies of end-linking in polydimethylsiloxane (PDMS) curing using 10 MHz shear waves, no drastic variation in G^* has been observed in the vicinity of the gel-point [Gandelsman *et al*., 1992]. However, a study of the same PDMS curing system using 10 MHz *longitudinal* waves has shown that the wave velocity increases during crosslinking, with a 'step-like' increase being recorded in the vicinity of the gel-point [Shefer *et al*., 1990].

These findings illustrate an important principle in relation to the application of high-frequency techniques: the greater success of longitudinal waves over shear waves in the studies mentioned above derives from the relative length scales of the structures (e.g. particle size or dimension of polymer molecule) and the wavelengths involved in measurements. At any frequency, the wavelength of longitudinal waves considerably exceeds that of shear waves, and the former may therefore be more appropriate for probing the development of long range structural details. Alternatively, lower frequency shear waves may be used [Hodgson and Amis, 1990]. In addition to techniques which exploit bulk longitudinal and transverse waves, *surface* waves have been used to study the sol–gel transition in gelatin [Takahashi and Choi, 1996].

Inevitably, the conjunction of frequency-dependent visco-elastic properties and wave propagation leads to consideration of visco-elastic wave dispersion and its influence on conventional wave-based measurements, such as those involving resonance phenomena and pulse propagation techniques.

2.8.1 Resonance-based techniques

Resonance phenomena provide a simple method of characterizing visco-elastic properties which does not require absolute determination of force, or precise setting of shearing gaps. Many high frequency devices based on resonance have been reported [Waterman, *et al*., 1979; Hausler *et al*., 1996; Stoimenova *et al*., 1996].

Basic aspects of the resonance technique may be illustrated by considering a linear visco-elastic medium between two parallel plates, one undergoing forced harmonic displacement, amplitude a $(= a_o \cos \omega t)$, the other being fixed. As ω is varied, resonances occur and a resonance bandwidth analysis yields the loss tangent, $\tan \delta$ [Whorlow, 1992; Ingard 1988].

The extent to which the resonance bandwidth analysis is susceptible to dispersion-induced errors has been considered and it has been established that serious errors may be incurred ($>1\%$ in δ) under conditions where waves are damped exponentially in one wavelength [Williams and Williams, 1994].

2.8.2 Pulse propagation techniques

Recourse to pulse propagation measurements is often prompted by their apparent simplicity, involving measurements of the 'time-of-flight' of a disturbance propagating through a visco-elastic material [Joseph *et al*., 1986].

In plane-harmonic shear-wave propagation in a linear medium of density ρ, G' and G'' are given by,

$$G' = \frac{\rho v^2 (1 - r^2)}{(1 + r^2)^2}; \tag{2.34a}$$

$$G'' = \frac{\rho v^2 \cdot 2r}{(1 + r^2)^2} \tag{2.34b}$$

[Ferry, 1980] where ω is the angular frequency in rad/s, $r = \lambda/(2\pi x_o)$ where λ is the shear wave length, x_o is the exponential damping length and v is the shear wave phase velocity. For known ω and ρ, G' and G'' may be obtained from equation 2.34 by measurement of v and x_o.

Such simple measurements belie the complicating effects of visco-elastic wave dispersion, which may render their analysis unreliable. The tendency of pulse frequency components to travel at different velocities in dispersive media distorts the pulse, thereby influencing measurements of damping to a degree dependent on the medium and the spectral content of the pulse. The latter, in turn, depend on pulse shape. This visco-elastic wave dispersion, associated with dissipative stresses, can severely restrict the application of pulse propagation techniques in which the measured velocity v_w may correspond to a *group* velocity, U, not the requisite *phase* velocity, v. As U and v may differ

significantly in visco-elastic media (in which $U > v$), serious over-estimates of elasticity may result.

In some instruments the phase velocity, v, is measured *directly* (using continuous shear waves), as in the 'virtual gap' rheometer, VGR, a multiple path shear wave interferometer which operates in the frequency range 100 Hz to *ca*. 2 kHz [Williams and Williams, 1992].