Rheology.

Oscillatory Shear measurements:

By subjecting a specimen to an oscillatory stress (σ) and determining the response, both the elastic and viscous or damping characteristics can be obtained.

The cone is forced into oscillatory shear (angular frequency ω) or rotation.
The sample is placed between the plate and the cone.

**Linear Viscoelasticity.**

When oscillatory shear measurements are performed in the linear viscoelastic regime, the storage modulus $G'$ (elastic response) and loss modulus $G''$ (viscous behavior) are independent of the strain amplitude.

*Viscosity experiments* are carried out in the zero-shear-rate Newtonian plateau (low shear rate).
Oscillatory Shear Experiments.

In an oscillatory shear experiment a sample, which is exposed to a sinusoidal strain (\(\gamma\)) at an angular frequency of \(\omega\) will respond with a gradual approach to a steady sinusoidal stress (\(\sigma\))

\[
\gamma = \gamma_0 \sin \omega t \tag{1}
\]

\[
\sigma = \gamma_0 (G'(\omega) \sin \omega t + G''(\omega) \cos (\omega t)) \tag{2}
\]

From this type of experiment the storage modulus \(G'\), the loss modulus \(G''\) and the dynamic viscosity \(\eta' = G''/\omega\) can be determined.
Loss tangent: \[ \tan \delta = \frac{G''}{G'} \] (measure of damping)

**Theoretical Models for Linear Viscoelasticity**

In the linear viscoelastic regime (small strain values) the viscoelastic properties of the incipient gel can be described by the gel equation (Winter and Chambon; J. Rheol. 1986, 30, 367)

\[ (-\infty < t' < t) \]

\[ m(t) = \int_{-\infty}^{t} (t - t')^n \gamma(t')dt' \]  \hspace{1cm} (3)

\( m = \) The shear stress

\( \gamma(t') = \) the rate of deformation of the sample
S = the gel strength parameter (depends on the crosslinking density and the molecular chain flexibility)

n = the relaxation exponent

For *incipient gels* $G'$ and $G''$ are expected to obey *power laws in frequency*

\[ G' \sim G'' \sim \omega^n \]  \hspace{1cm} (4)

The *gel point of a chemical gel* can be determined by observation of a *frequency-independent value of tan $\delta$ versus time or versus temperature for a thermoreversible gel.*
An alternative method is to plot against temperature the “apparent” viscoelastic exponents $n'$ and $n''$ obtained from the frequency dependence of $G'$ and $G''$ at each temperature of measurement and observing a crossover where $n'=n''=n$.

*Rheological features of a chemically cross-linked system:* Aqueous Poly(vinyl alcohol) (PVA) in the presence of Glutaraldehyde (GA).
The time of gelation decreases with increasing polymer concentration and cross-linker concentration.
The behavior at the gel-point:

At the gel point, the straight lines representing the frequency dependencies of $G'$ and $G''$ are parallel (log-log plot) and we may distinguish between three situations:
a) For chemical gels ("strong gels") one usually have $G' < G''$.

b) For stoichiometrically balanced chemical gels the dynamic moduli are usually congruent ($G' = G''$).

c) For physical gels we usually have ("weak" gels) $G' > G''$. 
The value of the viscoelastic exponent decreases with increasing polymer concentration and at low cross-linker concentration it also decreases as the cross-linker density increases. This trend is probably due to enhanced entanglement effects.
The gel strength parameter increases with polymer concentration and it rises with cross-linker density at low GA-concentrations.
Temperature-induced gelation of an EHEC/SDS sample:

\[ G' \sim \omega^{n'} \]
\[ G'' \sim \omega^{n''} \]

\[ T = 36 \, ^\circ C \quad n' = 0.40 \pm 0.01 \quad n'' = 0.40 \pm 0.01 \]

**Macromolecules** 31, 1852 (1998)