

Lecture 14: Linear viscoelasticity

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1 Suggested reading

- *Polymer Physics* – Rubinstein and Colby: Chapter 7
- *Viscoelastic Properties of Polymers* – Ferry

2 Viscoelasticity

The classic theory of elasticity describes the behavior and mechanical properties of elastic solids. In these materials, stress is directly proportional to strain for small deformations and independent of the strain rate, as described by Hooke's law. The classic theory of hydrodynamics describes the behavior of viscous liquids. In these materials, stress is directly proportional to the strain rate and independent of the magnitude of the strain, as described by Newton's law. These extremes are idealizations yet many engineering materials approximate ideal Hookean elastic solids or ideal Newtonian liquids at infinitesimally small strains or strain rates. However, with finite strains or strain rates many materials deviate from these ideal properties and some materials have aspects of a Hookean elastic solid and a Newtonian liquid embedded in their molecular structure. These latter materials exhibit **viscoelastic behavior** as they respond to deformation with both a viscous and an elastic response. In many of the materials that are used for modern engineering, viscoelastic behavior is negligible. However, the mechanical behavior of polymer solutions, networks, and gels is dominated by viscoelasticity and this remarkable phenomena remains an active field of research.

The importance of viscoelastic behavior in polymeric materials should not surprise us. Any deformation of the material induces deformation of the individual chains which is jiggling with thermal energy on the length scale of bonds, atoms, monomers, chain segments, and up to the whole chain. Upon deformation, the chain adopts a new configuration and the jiggling adapts to the new confirmation. The molecular motions at different length scales result in relaxation times on different time scales. In contrast, the deformation of a classic metal or crystalline solid results in the displacement of individual atoms away from an equilibrium position that induces a local restoring force according to the interatomic potential well. The elastic modulus of these materials can be predicted from the interatomic potentials. The deformation of a liquid composed of small molecules results in viscous flow that is characterized by the variation in the distribution of molecules interacting with a given molecule under stress. These rearrangements are local and, as with solids, the viscosity of a liquid can be calculated, in principle, from molecular information. Polymeric materials exhibit both elastic and viscous signatures and predicting these behaviors from molecular information is much more challenging. However, the inverse problem is more reasonable. Careful measurements of the viscoelastic behavior of a polymeric material can be used to elucidate structural features in the material including short- and long-range interactions as well as to assist in the engineering of functional polymeric materials for a range of applications.

3 Linear viscoelasticity

The mechanical properties of the networks and gels that we have been discussing exhibit are measured using linear viscoelasticity. One way to visualize the principles of linear viscoelasticity is to consider a simple shear geometry, in which the material is deformed between two flat and rigid surfaces separated by a distance h . We assume strong adhesion between the material and the surfaces such that no slippage occurs at these interfaces. The bottom surface is fixed and the top surface is free to move under a defined force f or a defined displacement Δx . If a force f is applied to the top surface the force will be transferred through the material (solid or liquid) and fixing the bottom surface requires an equal-and-opposite force $-f$ at the bottom surface.

We defined the **shear stress** σ_{xy} or σ as the ratio of the applied force to the cross-sectional area of the surfaces A :

$$\sigma \equiv \frac{f}{A}. \quad (1)$$

The **shear strain** γ is defined as the displacement of the top surface Δx over the separation gap h :

$$\gamma \equiv \frac{\Delta x}{h}. \quad (2)$$

With these definitions for stress and strain the entire sample experiences the identical shear stress and shear strain, assuming that the material deforms uniformly.

If we place an ideal elastic solid between the two surfaces, the shear stress σ will vary directly with the shear strain γ and the constant of proportionality is the **shear modulus** G :

$$G \equiv \frac{\sigma}{\gamma}. \quad (3)$$

Equation 3 is **Hooke's law of elasticity** and is generally valid for solids under small strain deformations. The SI unit for shear modulus is $\text{Pa} \equiv \text{kg m}^{-1} \text{s}^{-2}$.

If instead, we place an ordinary liquid, composed of small molecules, between the two surfaces the stress will vary directly with the shear rate $\dot{\gamma}$, which is defined as the rate of change of the shear strain with time:

$$\dot{\gamma} \equiv \frac{d\gamma}{dt}. \quad (4)$$

For ordinary liquids, the shear stress is directly proportional to the shear rate and the constant of proportionality is the **shear viscosity** η :

$$\eta \equiv \frac{\sigma}{\dot{\gamma}}. \quad (5)$$

Equation 5 is **Newton's law of viscosity** and this describes the behavior of Newtonian liquids. The SI unit for viscosity is Pa s .

As discussed above, polymeric materials are neither ideal elastic solids or simple liquids and instead demonstrate viscoelastic behavior. That is, they exhibit intermediate properties between Hookean solids and Newtonian liquids. A simple model of viscoelasticity is the **Maxwell model** that combines an ideal elastic element in series with a perfectly viscous element. The Maxwell model is also referred to as the spring-dashpot model. As the two elements are in series, the total shear strain is the sum of the strain in each element:

$$\gamma = \gamma_e + \gamma_v. \quad (6)$$

And the stress σ is the same in each element:

$$\sigma = G_M \gamma_e = \eta_M \frac{d\gamma_v}{dt}. \quad (7)$$

As the model contains a viscous element the material will have the ability to relax stress on certain time scales. The **relaxation time** τ_M for a Maxwell material is the ratio of the viscosity of the viscous element η_M to the modulus of the elastic element G_M :

$$\tau_M \equiv \frac{\eta_M}{G_M}. \quad (8)$$

On time scales shorter than the relaxation time the material behaves like a solid and on time scales longer than the relaxation time the material flows like a liquid. In principle, the networks and gels that we are studying have viscoelastic properties and behave in part as a solid and in part as a liquid and the relative response can depend on the time scale of which we probe or observe the material.

4 Boltzmann superposition principle

By definition, the material properties of viscoelastic materials are time dependent. As one example, we can consider applying a step strain of magnitude γ at time $t = 0$ on the material. If we have a perfectly elastic solid, the stress would jump to $G\gamma$ and remain there while the strain is applied. If we have a perfectly viscous liquid, there would be a transient stress response that would spike and instantaneously decay to zero stress. In viscoelastic networks and gels, the stress following a step strain will have some time dependence $\sigma(t)$. We define the **stress relaxation modulus** $G(t)$ as the remaining stress in the material at time t divided by the magnitude of the step strain γ :

$$G(t) \equiv \frac{\sigma(t)}{\gamma}. \quad (9)$$

This is a time-dependent variant of Hooke's law and the stress relaxation modulus decays on the time scale of the relaxation time τ_M of the material to G_{eq} for a viscoelastic solid and 0 for a viscoelastic liquid.

At sufficiently small values of the applied strain γ , the stress relaxation modulus behaves linearly and is independent of strain. Therefore, doubling the strain in the linear region will double the stress. A consequence of this **linear viscoelastic** behavior, is that the stress from any combination of small step strains is a simple linear combination of the stresses that result from each individual strain $\delta\gamma_i$ at time t_i :

$$\sigma(t) = \sum_i G(t - t_i)\delta\gamma_i. \quad (10)$$

More simply, Equation 10 states that, in the linear response regime, the stress that results from each strain is independent of all the other strains. The system still remembers the previous strains and relaxes accordingly as new strains are applied. The stress relaxation modulus informs how much stress remains at time t from the past deformation $\delta\gamma_i$ over the elapsed time $(t - t_i)$. Further, Equation 10 can be transformed from strain space to time space using the definition of shear rate in Equation 4, which implies $\delta\gamma_i = \dot{\gamma}_i\delta t_i$:

$$\sigma(t) = \sum_i G(t - t_i)\dot{\gamma}_i\delta t_i. \quad (11)$$

In the case of a smooth strain history, Equation 11 can be reformulated as an integral over all previous strains.

$$\sigma(t) = \int_{-\infty}^t G(t - t')\dot{\gamma}_i(t')dt'. \quad (12)$$

We integrate from $t = -\infty$ as we must account for all past strains to ensure that the whole history is accounted for. Thus, the stress in a material is the result of all past deformations and the memory of each prior deformation decays as the relaxation modulus decays, which is on the time scale of the relaxation time of the material.

5 Oscillatory dynamic mechanical analysis

One of the simplest and most common techniques to quantify the viscoelasticity of polymeric materials is oscillatory dynamic mechanical analysis, often using a **shear rheometer**. In this approach, a sinusoidal strain with an angular frequency ω is applied to the sample:

$$\gamma(t) = \gamma_0 \sin(\omega t). \quad (13)$$

Here, γ_0 is the shear strain amplitude. The standard geometries for a shear rheometer are parallel plates, cone and plate, or Couette cells. A major advantage of the oscillatory approach, is that it can easily probe the viscoelastic response of the material on different time scales ($\tau \propto \frac{1}{\omega}$) by varying the angular frequency ω .

If a perfectly elastic solid is investigated in oscillatory shear, then the stress in the sample can be related to the strain using Hooke's law:

$$\sigma(t) = G\gamma(t) = G\gamma_0 \sin(\omega t). \quad (14)$$

Here, the stress is perfectly in-phase with the deformation.

In contrast, if a Newtonian liquid is investigated in oscillatory shear, the stress in the sample can be related to the shear rate using Newton's law:

$$\sigma(t) = \eta \frac{d\gamma(t)}{dt} = \eta\gamma_0\omega \cos(\omega t) = \eta\gamma_0\omega \sin\left(\omega t + \frac{\pi}{2}\right). \quad (15)$$

Here, the stress oscillates with the same frequency ω but it is out-of-phase by $\frac{\pi}{2}$.

The mechanical response of a viscoelastic material is between that of a Hookean solid and a Newtonian liquid. The linear stress response of a viscoelastic material will also oscillate at the frequency of the applied strain, but the stress is phase-shifted from the strain by a **phase angle** δ :

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta). \quad (16)$$

The phase angle δ can take any value in the range $0 \leq \delta \leq \frac{\pi}{2}$ [for a Hookean solid $\delta = 0$ and for a Newtonian liquid $\delta = \frac{\pi}{2}$] and can depend on the applied frequency. Thus, we can decompose the stress response into two orthogonal components that each oscillate with the frequency ω , one component that is in-phase $\delta = 0$ and one component that is out-of-phase $\delta = \frac{\pi}{2}$:

$$\sigma(t) = \gamma_0[G'(\omega) \sin(\omega t) + G''(\omega) \cos(\omega t)]. \quad (17)$$

We define $G'(\omega)$ as the **storage modulus** or **elastic modulus** and it is a measure of the elastic response of the material, or how much of the strain energy is stored by the material. We define $G''(\omega)$ as the **loss modulus** or **viscous modulus** and it is a measure of the viscous response of the material, or how much of the strain energy is dissipated by the material. As indicated by the formulation, $G'(\omega)$ and $G''(\omega)$ both depend on the frequency of the oscillatory shear.

Equation 17 can be related to Equation 16 using the trigonometric identity for the sine of a sum:

$$\sin(\omega t + \delta) = \cos \delta \sin(\omega t) + \sin \delta \cos(\omega t). \quad (18)$$

Therefore, we can relate G' and G'' to the phase angle δ and the modulus amplitude $\frac{\sigma_0}{\gamma_0}$ for each frequency ω :

$$G' = \frac{\sigma_0}{\gamma_0} \cos \delta, \quad (19)$$

$$G'' = \frac{\sigma_0}{\gamma_0} \sin \delta. \quad (20)$$

We can then relate the tangent of the phase angle δ to the ratio of G'' to G' :

$$\tan \delta = \frac{G''}{G'}. \quad (21)$$

We define $\tan \delta$ as the **loss tangent** of the material. In general, when $\tan \delta < 1$ we consider the material to be acting as a viscoelastic solid at that frequency and when $\tan \delta > 1$ we consider the material to be acting as a viscoelastic liquid at that frequency. In total, oscillatory shear is a powerful tool to investigate the viscoelastic properties of networks and gels and is used extensively in current research.