

Viscoelasticity

References

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1. Newton's law of viscous deformation

Subject to a load, a liquid flows. The amount of deformation is time-dependent and unlimited. When the load is removed, the liquid does not recover its original shape. The liquid has no memory.

To characterize such deformation, we subject the liquid to a state of shear stress τ , and then measure the shear strain γ as a function of time t . The record, $\gamma(t)$, allows us to calculate the strain rate $d\gamma/dt$. For some liquids, we may be able to fit the experimental data to a linear relation between the strain rate and the stress. If we can, we write

$$\frac{d\gamma}{dt} = \frac{\tau}{\eta}.$$

This linear fit is known as Newton's law of viscous deformation. (Some people's names simply stick whatever they do.) The fitting parameter, η , is known as the viscosity of the liquid. The viscosity has the dimension of time \times stress, and is specific to each liquid; e.g., water ($\eta \sim 10^{-3}$ sPa) and glass ($\eta \sim 10^{12}$ sPa).

2. Arrhenius equation

For a given liquid, the viscosity decreases as the temperature increases. A liquid flows when molecules pass one another, a process that is thermally activated. Thus, the relation between the viscosity and the temperature is often fit to the Arrhenius equation

$$\eta = \eta_0 \exp\left(\frac{q}{kT}\right).$$

The pre-factor η_0 and the activation energy q are parameters used to fit experimental data. kT is the temperature in units of energy. If we would rather use the Kelvin (K) as the unit for temperature, the conversion factors between the Kelvin and common units of energy is $k = 1.38 \times 10^{-23} \text{ JK}^{-1} = 8.63 \times 10^{-5} \text{ eVK}^{-1}$. We may measure the viscosity of a liquid at several temperatures, and then plot the data on the Arrhenius plot, namely, $\log \eta$ vs. $1/kT$. The activation energy is found from the slope of the plot, and the pre-factor η_0 the intercept.

3. A liquid subject to a multiaxial state of stress

Newton's law of viscosity is analogous to Hooke's law of elasticity. (I don't know who copied who in this case.) Following an analogous procedure, we may generalize Newton's law to a multi-axial state of stress, σ_{ij} . Often a liquid is taken to be incompressible; the volumetric strain is typically small compared to the shear strain.

Let $\mathbf{v}(x_1, x_2, x_3)$ be the velocity field. The strain rate is a tensor d_{ij} , given by

$$d_{ij} = \frac{1}{2} \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right)$$

The components of the stress relate to the components of the strain rate as

$$\sigma_{ij} = \eta \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) + \frac{1}{3} \sigma_{kk} \delta_{ij} = 2\eta d_{ij} + \frac{1}{3} \sigma_{kk} \delta_{ij}.$$

This is analogous to the generalized Hooke's law.

As a special case, under a uniaxial stress σ , the axial strain rate $d\varepsilon / dt$ relates to the stress as

$$\sigma = 3\eta \frac{d\varepsilon}{dt}.$$

The quantity $H = 3\eta$ defines the viscosity under uniaxial tension.

4. Types of deformation

How a material deforms depends on the constitution of the material. We can typically distinguish the following types of behavior:

Elastic strain. Under a load, the solid deforms instantaneously. Upon load removal, the solid recovers its original shape instantaneously. Deformation occurs as a result of bond stretching in crystals or chain straightening in rubbers (cross-linked polymers). Molecules do not change neighbors. Pictorial Representation: The spring. The experimental data is fit to

$$\varepsilon = \sigma / E .$$

Viscous strain. Under a load, a material deforms indefinitely. Molecules change neighbors. Pictorial Representation: The dashpot. The experimental data is fit to

$$\sigma = H \frac{d\varepsilon}{dt}$$

Plastic strain. The body does not recover its original shape when the load is removed. Dislocation motion. Crystal rearranges. Atoms change neighbors. Strain is zero when $\sigma < \sigma_Y$, indefinite when $\sigma > \sigma_Y$. Pictorial Representation: A sliding block. Static friction.

Elastic-plastic model. Spring in series with a frictional block. Iso-stress. The total strain is the sum of the elastic strain (displacement of the spring) and the plastic strain (displacement of the block).

Thermal strain. The body expands or contracts when the temperature changes. Anharmonic energy well. Pictorial Representation: The spring changes length upon temperature change. Experimental data are often fit to

$$\varepsilon = \alpha (T - T_{ref}) .$$

5. Linear viscoelasticity

1. Creep test of a viscoelastic rod

A rod of a polymer is held at a constant temperature, stress free, for a long time, so that its length no longer changes with time. The rod is in a state of equilibrium. At time zero, we attach a weight to the rod, and record its elongation as a function of time. Thus, the stress in the rod is a

step function of time. The rod is on its way from one equilibrium state to another equilibrium state. The strain is an increasing function of time, with the following characteristics:

1. *Unrelaxed strain, ϵ_U* . Instantaneous after we hang the weight to the rod, the rod elongates by a certain amount.
2. *Relaxed strain, ϵ_R* . After some time, the molecules reach a new equilibrium configuration, and the strain no longer changes with time. This is different from a polymer melt or any liquid.
3. *Relaxation time, τ* . The time scale to attain the relaxed strain. The time needed for the rod to change from the old to the new equilibrium state.

Sketch the function $\epsilon(t)$, and mark the above quantities.

To a first approximation, you may fit the record of the history of strain, $\epsilon(t)$, to a function

$$\epsilon(t) = \epsilon_U + (\epsilon_R - \epsilon_U) \left[1 - \exp\left(-\frac{t}{\tau}\right) \right].$$

We all do curve fitting, but some of us are more sophisticated. (We are all in the gutter, but some of us are looking at the stars. Oscar Wilde).

A molecular picture may look like this. When a weight is put on, molecules change configurations by two processes. A fast process occurs right after the weight is put on. A slow process takes place over some time. Of course, a polymer may have more than two processes, and the experimental record of $\epsilon(t)$ may not fit to the above formula.

2. Creep compliance

The magnitude of the strain should increase with the weight that we hang to the rod. Say at time zero we load two identical rods, one with weight W , and the other with weight $2W$. At any given time, the elongation of the second rod is twice that of the first rod. This linearity holds when the weight is small. We fit this experimental observation by

$$\epsilon(t) = D(t) \sigma,$$

where σ is the suddenly applied stress, $\varepsilon(t)$ is the strain as a function of time, and $D(t)$ is the compliance as a function of time. We can reinterpret the features of the function $\varepsilon(t)$, and denote the unrelaxed compliance by D_U , and the relaxed compliance by D_R . We may fit the experimental record with a formula:

$$D(t) = D_U + (D_R - D_U) \left[1 - \exp\left(-\frac{t}{\tau}\right) \right].$$

3. Spring-dashpot models

We next try to interpret the experimental observations. Your basic instinct might tell you to look how molecules pass one another, and try to relate various parameters to all the moving and jamming of the molecules. This approach has been tried as long as the existence of molecules was first appreciated, and has been dubbed as multi-scale modeling in recent years. The approach, however, is time consuming, and often not very practical. If you suspend your basic instinct for the time being, you may learn something from simple spring-dashpot models.

Maxwell model. This model represents a material with a spring in series with a dashpot. Because the two elements, the spring and the dashpot, are subject to the same stress, the model is also known as an iso-stress model. The total strain is the sum of the elastic and the viscous strain, so that

$$\frac{d\varepsilon}{dt} = \frac{1}{E} \frac{d\sigma}{dt} + \frac{\sigma}{H}.$$

This is an ODE. For a prescribed history of stress, the ODE can determine the history of strains. For example, in the creep test we prescribe the history of stress as a step function:

$$\sigma(t) = \begin{cases} 0, & t < 0 \\ \sigma, & t \geq 0 \end{cases}$$

The history of the strain will be

$$\varepsilon(t) = \begin{cases} 0, & t < 0 \\ \frac{\sigma}{E} + \frac{\sigma}{H}t, & t \geq 0 \end{cases}$$

We may also write the expression as

$$\varepsilon(t) = \frac{\sigma}{E} \left(1 + \frac{t}{\tau} \right),$$

where $\tau = H / E$ is a time scale. The model gives relaxation modulus:

$$D(t) = \frac{1}{E} \left(1 + \frac{t}{\tau} \right).$$

The Maxwell model gives an unrelaxed strain, but not a relaxed strain. The dashpot is unconstrained: the rod will flow indefinitely under the weight, and will never attain an equilibrium state. The long-time behavior is liquid-like.

Kelvin model. This model represents a material with a spring in parallel with a dashpot. Because the two elements are subject to the same strain, the model is also known as an iso-strain model. The total stress is the sum of the stress in the spring and the stress in the dashpot, so that

$$\sigma = E\varepsilon + H \frac{d\varepsilon}{dt}.$$

This equation relates a history of stress to a history of strain.

In the creep test, the stress is zero when $t < 0$, and is held at a constant level σ when $t > 0$. We now try to solve for the history of strain, $\varepsilon(t)$. The above equation becomes an inhomogenous ODE with constant coefficients. The general solution is

$$\varepsilon(t) = \frac{\sigma}{E} + A \exp\left(-\frac{t}{\tau}\right),$$

where A is a constant of integration, and $\tau = H / E$ is the relaxation time. At $t = 0$, the dashpot allows no strain, $\varepsilon(0) = 0$. This initial condition determines the constant A , so that the history of strain is

$$\varepsilon(t) = \frac{\sigma}{E} \left[1 - \exp\left(-\frac{t}{\tau}\right) \right].$$

The strain is linear in the stress, and the creep compliance is

$$D(t) = \frac{1}{E} \left[1 - \exp\left(-\frac{t}{\tau}\right) \right].$$

The Kelvin model gives a relaxed strain, but not an unrelaxed strain. In parallel, the spring cannot elongate instantaneously, and dashpot stops elongate eventually. The long-time behavior is solid like.

Zener model. Neither the Maxwell nor the Kelvin model is sufficient to describe the representative experimental data. To describe the above observations, we need a combination of the Maxwell and the Kelvin model. In the Zener model, a spring of compliance $D_R - D_U$ and a dashpot of viscosity H are in parallel, and form a Kelvin unit. The unit is then in series with another spring of compliance D_U . Let ε_1 be the strain due to the Kelvin unit, so that

$$\sigma = \frac{\varepsilon_1}{D_R - D_U} + H\dot{\varepsilon}_1.$$

The total strain $\varepsilon(t)$ is the sum of the strain due to the Kelvin unit and the strain due to the spring in series:

$$\varepsilon = \varepsilon_1 + D_U \sigma$$

For the creep test, the total strain is

$$\varepsilon(t) = D_U \sigma + (D_R - D_U) \left[1 - \exp\left(-\frac{t}{\tau}\right) \right] \sigma,$$

where the relaxation time is $\tau = H(D_R - D_U)$. The creep compliance is

$$D(t) = D_U + (D_R - D_U) \left[1 - \exp\left(-\frac{t}{\tau}\right) \right]$$

4. Stress varies as a function of time

Now we load a rod with a known history of stress, $\sigma(t)$. What will the history of strain, $\varepsilon(t)$, be? Of course, we can always measure the history of strain experimentally for each given history of stress, but that is a lot of measurements. We now describe a linear superposition principle.

Say we have conducted a creep test and measured the creep compliance, $D(t)$. In general the creep compliance is zero when $t < 0$, and increases when $t > 0$. Remember, $D(t)$ is measured by subject the solid to a step stress.

We next approximate a history of stress by a series of steps of stress:

- At time $t = u_0$, the stress steps from zero to σ_0 .
- At time $t = u_1$, the stress makes an additional step $\sigma_1 - \sigma_0$
- At time $t = u_2$, the stress makes yet another step $\sigma_2 - \sigma_1$

The total strain is the sum of the strains due to all the steps:

$$\varepsilon(t) = \sigma_0 D(t - u_0) + (\sigma_1 - \sigma_0) D(t - u_1) + (\sigma_2 - \sigma_1) D(t - u_2).$$

As an example, consider a rod subject to a stress at time zero. The stress is kept constant for a while and then removed at time t_1 . The rod gradually contracts to its original length. The stress is zero when $t < 0$, held at a constant level σ between $0 < t < t_1$, and dropped to zero again at $t > t_1$. The history of strain will be

$$\varepsilon(t) = \sigma D(t) - \sigma D(t - t_1).$$

At time zero, the strain steps up by $D_U \sigma$, and then increases with time. At time t_1 , the strain steps down by $D_U \sigma$, and then gradually decays to zero.

Boltzmann superposition principle: A rod is held at a constant temperature, stress free, for a long time, and no longer changes its length. This length is used as the reference to calculate the strain. We then apply a history of stress $\sigma(t)$. The history of strain is given by a superposition:

$$\varepsilon(t) = \int_{-\infty}^t D(t-u) \frac{d\sigma}{du} du$$

In this equation, t is the time at which the strain is measured, and u is the variable of integration (i.e., a dummy variable). The lower limit of the integral is $-\infty$ because the complete stress history prior to t contributes to the observed strain. The upper limit of the integral is t , because the stress applied after t should have no effect on the strain measured at time t .

5. The temperature-dependence of creep.

Creep is a thermally activated process. When the creep test is conducted at a higher fixed temperature, the relaxation time is shorter. This temperature dependence may be understood using any of the spring dashpot models. For example, let us look at the Zener model. Take that the compliances of the two springs are temperature independent. The viscosity decreases as the temperature increases, and may fit the Arrhenius equation

$$H = H_0 \exp\left(\frac{q}{kT}\right),$$

where the pre-factor H_0 and the activation energy q are parameters used to fit the experimental data. Recall the relaxation time in the Zener model is given by $\tau = H(D_R - D_U)$. Thus, the relaxation time fits the Arrhenius equation,

$$\tau = \tau_0 \exp\left(\frac{q}{kT}\right).$$

The shift factor: A real polymer may not fit with the Zener model. Rather, the temperature effect is implemented by a shift factor. Denote the creep compliance at temperature T_0 by $D_{T_0}(t)$, and the creep compliance at temperature T by $D_T(t)$. Plot D_{T_0} and D_T as function of $\log t$. Each curve has two plateaus, one corresponding to the short-time unrelaxed compliance, the other corresponding to the long-time, relaxed compliance. These plateaus are approximately independent of time. The two curves are approximately identical after a horizontal shift. That is

$$D_T(t) = D_{T_0}\left(\frac{t}{a_T}\right)$$

where a_T is called the shift factor: The curves D_{T_0} and D_T as function of $\log t$ shift by $\log a_T$.

If we assume the Arrhenius equation for the relaxation time, the shift factor is given by

$$a_T = \exp\left[\frac{q}{k}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right].$$

Creep of a real polymer may involve several activated processes, each with its own activation energy. Consequently, the shift factor may show other temperature dependence.

Accelerated test: The above shifting relation says that the creep compliance at a long time and a low temperature is the same as the creep compliance at a short time and a high temperature. Relations like this are known as the *time-temperature correspondence*, and form the basis for accelerated tests, which are widely practice in industries. You can shorten the time of testing by increasing the temperature. With the correspondence, you can use the short-time response measured at a high temperature to predict the long-time response at a low temperature.

6. Thermal strain upon sudden change in temperature

A rod is held at a temperature T_{ref} for a long time, so that its length no longer changes with time. At time zero, the temperature is changed from T_{ref} to T , and is subsequently held constant. We measure the length of the rod as a function of time. Write

$$\varepsilon(t) = \alpha_T(t)(T - T_{ref}).$$

We expect the coefficient of thermal expansion to be a function of both time and temperature.

We can get some feel for the CTE by using Zener's model again. Let α_U be the CTE of the spring in series, and $\alpha_R - \alpha_U$ be the CTE of spring in parallel with the dashpot. The dashpot undergoes no thermal strain. Let ε_1 be the strain due to the Kelvin unit. When the temperature increases, the spring thermally expands, but the dashpot cannot respond immediately. Consequently, the spring will be in compression, and the dashpot will be in tension. Because no net stress is applied, the sum of the stresses in the two elements must vanish:

$$0 = \frac{\varepsilon_1 - (\alpha_R - \alpha_U)(T - T_{Ref})}{D_R - D_U} + H\dot{\varepsilon}_1.$$

The total strain is the sum of the strain due to the Kelvin unit and the strain due to the spring in series:

$$\varepsilon = \varepsilon_1 + \alpha_U(T - T_{Ref}).$$

Solving this ODE, we obtain the CTE as a function of time.

$$\alpha_T(t) = \alpha_U + (\alpha_R - \alpha_U) \left[1 - \exp\left(-\frac{t}{\tau}\right) \right],$$

where $\tau = H(D_R - D_U)$. This relation is the same as that of the creep compliance.

For a viscoelastic material, the CTE is sensitive to temperature. We can use the same shift factor a_T to relate CTEs measured in two experiments, one with the temperature changed from T_{ref} to T_0 , and the other with the temperature changed from T_{ref} to T . Thus,

$$\alpha_T(t) = \alpha_{T_0} \left(\frac{t}{a_T} \right).$$

Thermal strain subject to time-dependent temperature: Now we combine the two ideas: The Boltzmann superposition principle and the shift factor. A rod is held at a temperature T_{ref} for a long time, so that its length no longer changes with time. This length is set to be the reference in calculating the strain. The rod is then subject to a history of temperature, $T(t)$. The history of strain is

$$\varepsilon(t) = \int_{-\infty}^t \alpha_{T_0}(\xi) \frac{dT}{du} du,$$

where the “shifted” time is

$$\xi = \int_u^t \frac{dt'}{a_T[T(t')]}.$$

An algorithm to calculate the history of strain in a rod subject to known histories of stress and temperature. A rod is held at a temperature T_{ref} for a long time, so that the length of the rod no longer changes with time. This length is set to be the reference in calculating the strain. The rod is then subject to histories of temperature and stress, $T(t)$ and $\sigma(t)$. The history of strain is

$$\varepsilon(t) = \int_{-\infty}^t \left[D_{T_0}(\xi) \frac{d\sigma}{du} + \alpha_{T_0}(\xi) \frac{dT}{du} \right] du.$$

The “shifted” time ξ is

$$\xi = \int_u^t \frac{dt'}{a_T[T(t')]}.$$

The shift factor is a function of temperature, $a_T(T)$.

In summary, for a give polymer, once the creep compliance is measured at one temperature, $D_{T_0}(t)$, the CTE is measured for one change in temperature, $\alpha_{T_0}(t)$, and the shift factor is measured perhaps by creep tests at several temperatures, the above algorithm allows us to calculate the history of strain under any prescribed histories of temperature and stress.

7. Relaxation test

At time zero, apply a constant strain to a rod, and then record the stress in the rod as a function of time. The stress decreases as a function of time. Main characteristics include

1. σ_U the unrelaxed stress is obtained instantaneously after the application of the step-strain.
2. σ_R the relaxed stress is obtained after a long time of the application of the step-strain.
3. β is the characteristic time for stress relaxation. For the same material, the characteristic time for stress relaxation test is different from the characteristic time for the creep test.

If the applied strain is sufficiently small, the stress is linear in the strain, namely,

$$\sigma(t) = E(t)\epsilon$$

The stress relaxation modulus is a function of time, $E(t)$. A suitable curve to fit the experimental data may be

$$E(t) = E_R + (E_U - E_R) \exp\left(-\frac{t}{\beta}\right).$$

From physical considerations, the compliance and the modulus at the two limit states are related:

$$E_U = 1/D_U, \quad E_R = 1/D_R.$$

Zener's model relates the relaxation time for the two kinds of tests (step-stress, and step-strain):

$$\tau/\beta = E_U/E_R.$$

The effect of time-dependent strain. At time $-\infty$, both stress and strain are zero. Prescribe a history of strain $\epsilon(u)$, where u represents time, and the strain can be nonzero since $u = -\infty$. Let $E(t)$ be the relaxation modulus. The history of stress is given by a superposition:

$$\sigma(t) = \int_{-\infty}^t E(t-u) \frac{d\varepsilon}{du} du$$

In this equation, t is the time at which the stress is measured, and u is the integration variable. The lower limit of the integral is $-\infty$, because the complete strain history prior to t contributes to the observed stress. The upper limit of the integral is t , because the strain applied after t should have no effect on the stress measured at time t .

A rod loaded at a constant strain rate. As an example, consider that case that a testing machine is programmed to apply strain at a constant rate, $\varepsilon(t) = kt$, where k is the rate of strain. Plot $E(t)$, $\varepsilon(t)$ and $\sigma(t)$. We should expect a nonlinear stress-strain relation. Use Boltzmann's superposition principle to obtain the stress history:

$$\sigma(t) = \int_0^t E(t-u) \frac{d\varepsilon}{du} du.$$

Note $d\varepsilon/du = k$. Change variable, $v = t - u$, and we obtain that

$$\sigma(t) = k \int_0^t E(v) dv.$$

Note that

$$\bar{E}(t) = \frac{1}{t} \int_0^t E(v) dv$$

is the average modulus between time 0 and t . We have

$$\sigma(t) = \bar{E}(t) \varepsilon(t).$$

Because the average modulus decreases with time, the stress-strain relation is sub-linear.

8. Cyclic stress and strain and the phase angle

At a constant temperature, program a loading machine to prescribe to a rod a cyclic history of strain:

$$\varepsilon(t) = \varepsilon_0 \sin \omega t.$$

Here ε_0 is the amplitude, and ω the frequency. The strain repeats itself after a period of time equal to $2\pi/\omega$. What will be the stress as a function of time? The answer depends on what kind of materials the rod is made of.

For a *purely elastic solid*, the stress is proportional to the strain at all time, $\sigma(t) = E\varepsilon(t)$, where Young's modulus E is a constant. Consequently, when the machine prescribes a sinusoidal strain $\varepsilon(t) = \varepsilon_0 \sin \omega t$ to the rod, the stress in the rod is

$$\sigma(t) = E\varepsilon_0 \sin \omega t .$$

The stress amplitude is linear in the strain amplitude, $\sigma_0 = E\varepsilon_0$. The stress response replicates the strain input at all time. That is, the stress is *in phase* with the strain.

For a *purely viscous solid*, the stress is proportional to the strain rate, $\sigma(t) = \eta d\varepsilon / dt$. The viscosity η is a constant independent of time. Consequently, when the machine is programmed to apply a sinusoidal strain $\varepsilon(t) = \varepsilon_0 \sin \omega t$ to the solid, the stress in the solid is $\sigma(t) = \eta\varepsilon_0 \omega \cos \omega t$. This expression can be rewritten as

$$\sigma(t) = \eta\varepsilon_0 \omega \sin\left(\omega t + \frac{\pi}{2}\right)$$

The stress amplitude is linear in the strain amplitude, $\sigma_0 = \eta\omega\varepsilon_0$. The stress is out of phase with the strain; for a purely viscous solid, the stress leads the strain by a phase angle $\pi/2$.

Now consider a *viscoelastic solid*. When the machine dictates the solid to strain according to $\varepsilon(t) = \varepsilon_0 \sin \omega t$, the stress as a function of time looks complicated in the first few cycles. Afterwards, the stress becomes cyclic, with the same frequency ω , but with a phase shift. This cyclic stress is written as

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

The phase shift δ is between 0 and $\pi/2$.

Energy recovery and energy loss: Let L be the length of the polymer rod, and A the cross-sectional area. When the machine strain the solid according to $\varepsilon(t) = \varepsilon_0 \sin \omega t$, the solid elongates as

$$\Delta(t) = L\varepsilon_0 \sin \omega t .$$

The stress in the rod is $\sigma(t) = \sigma_0 \sin(\omega t + \delta)$. Recall an identity of trigonometry, $\sin(\omega t + \delta) = \sin \omega t \cos \delta + \cos \omega t \sin \delta$. The force of the machine on the solid is

$$F(t) = A\sigma_0 (\sin \omega t \cos \delta + \cos \omega t \sin \delta).$$

During a time interval dt , the solid elongates by $d\Delta$, and the machine does work

$$Fd\Delta = F \frac{d\Delta}{dt} dt$$

to the solid. In one full cycle the machine does work

$$\int_0^{2\pi/\omega} F \frac{d\Delta}{dt} dt = AL \int_0^{2\pi/\omega} \sigma_0 (\sin \omega t \cos \delta + \cos \omega t \sin \delta) (\varepsilon_0 \omega \cos \omega t) dt = \pi AL \sigma_0 \varepsilon_0 \sin \delta$$

In a complete cycle, the elastic energy stored in the rod repeats its value. Consequently, the net work done by the machine in a complete cycle must all become heat. The above expression is the energy dissipated by the solid per cycle.

The power (energy per unit time) dissipation per unit volume is

$$\frac{1}{2} \omega \varepsilon_0 \sigma_0 \sin \delta.$$

For a purely elastic solid, the stress is in phase with the strain, $\delta = 0$, and no energy is dissipated. For a purely viscous solid, the stress is out of phase with strain, $\delta = \pi/2$, and above formula gives the power dissipated.

Storage modulus and loss modulus. When a linearly viscoelastic material is subject to the cyclic strain, $\varepsilon(t) = \varepsilon_0 \sin \omega t$, the history of stress is

$$\sigma(t) = \sigma_0 \sin \omega t \cos \delta + \sigma_0 \cos \omega t \sin \delta$$

Define

$$E' = \frac{\sigma_0 \cos \delta}{\varepsilon_0}, \quad E'' = \frac{\sigma_0 \sin \delta}{\varepsilon_0}.$$

The two moduli are independent of the amplitude of the strain, ε_0 . When the rod is subject to the cyclic strain $\varepsilon(t) = \varepsilon_0 \sin \omega t$, the cyclic stress in the rod can be written as

$$\sigma(t) = \varepsilon_0 (E' \sin \omega t + E'' \cos \omega t)$$

The stress is the sum of an in-phase response and out-of-phase response. We call E' storage modulus, and E'' loss modulus. The in-phase stress and strain results in elastic energy, which is completely recoverable. The $\pi/2$ out-of-phase stress and strain results in the dissipated energy.

The loss tangent is defined as

$$\tan \delta = \frac{E''}{E'}.$$

Both the storage modulus and the loss modulus are functions of the loading frequency. Write the two functions as $E'(\omega)$ and $E''(\omega)$. The following experimental observations conform to our intuition about visco-elasticity.

1. When the loading frequency is low, $\omega \rightarrow 0$, the storage modulus is the same as the relaxed modulus, $E'(0) = E_R$, and the loss modulus vanishes, $E''(0) = 0$. How low a frequency is low? The loading frequency should be compared with the material time scale, the relaxation time, β . The frequency is low when $\beta\omega \ll 1$.
2. When the loading frequency is high, $\beta\omega \gg 1$, the storage modulus is the same as the unrelaxed modulus, $E'(\infty) = E_U$, and the loss modulus vanishes $E''(\infty) = 0$.
3. At intermediate some frequency, the storage modulus increases rapidly, and the loss modulus peaks.

Complex variables. Recall Euler's identity:

$$\exp(i\theta) = \cos \theta + i \sin \theta.$$

Write complex strain as

$$\varepsilon^* = \varepsilon_0 \exp(i\omega t).$$

We can use this expression in algebra and in solving ODE. At the end of the calculation, we will just take the imaginary part, which gives $\varepsilon(t) = \varepsilon_0 \sin \omega t$.

Let E^* be the *complex modulus*, defined as

$$E^* = E' + iE''.$$

The complex modulus is a function of the loading frequency, $E^*(\omega)$. The complex stress is linear in the complex strain,

$$\sigma^* = E^* \varepsilon^*.$$

Recall the definitions of the storage modulus and the loss modulus, and we have

$$E^* = E_0 \exp(i\delta),$$

with $E_0 = \sigma_0 / \varepsilon_0$. Consequently, the stress becomes $\sigma^* = \sigma_0 \exp(i\omega t + i\delta)$. Taking the imaginary part, we recover the stress $\sigma(t) = \sigma_0 \sin(\omega t + \delta)$.

Compliance representation. The cyclic experiment can also be represented in terms of compliance. Let stress history be $\sigma = \sigma_0 \sin \omega t$. The strain history must be delayed by a phase factor δ . That is, $\varepsilon = \varepsilon_0 \sin(\omega t - \delta)$. Define two kinds of compliances:

$$D' = \frac{\varepsilon_0 \cos \delta}{\sigma_0}, \quad D'' = \frac{\varepsilon_0 \sin \delta}{\sigma_0}.$$

and the complex compliance $D^* = D' - iD''$. In the complex representation, when the stress history is $\sigma^* = \sigma_0 \exp(i\omega t)$, the strain history is

$$\varepsilon^* = D^* \sigma^*.$$

Note that $E^*(\omega) = 1/D^*(\omega)$.

The Zener model. Compliance as a function of the loading frequency. Recall the ODE for the Zener model:

$$\sigma = \frac{\varepsilon_1}{D_R - D_U} + H\dot{\varepsilon}_1, \quad \varepsilon = \varepsilon_1 + D_U \sigma$$

Let $\sigma^* = \sigma_0 \exp(i\omega t)$ and $\varepsilon^* = \sigma_0 D^* \exp(i\omega t)$. We find that

$$D^* - D_U = \frac{D_R - D_U}{1 + i\omega\tau},$$

where $\tau = H(D_R - D_U)$. Taking the real and the imaginary part, we have

$$D'(\omega) = D_U + \frac{D_R - D_U}{1 + (\omega\tau)^2}, \quad D''(\omega) = \frac{(D_R - D_U)\omega\tau}{1 + (\omega\tau)^2}$$

1. When the loading frequency is low $\omega\tau \ll 1$, the storage compliance is the same as the relaxed compliance, and the loss compliance vanishes.
2. When the loading frequency is high $\omega\tau \gg 1$, the storage compliance is the same as the unrelaxed compliance, and the loss compliance also vanishes.
3. When $\omega\tau \sim 1$, the storage compliance decreases rapidly with ω , and the loss compliance peaks.

9. A general relation between modulus measured under various tests

The Boltzmann superposition principle allows us to relate compliance and modulus measured under various testing conditions. Say we know the relaxation modulus $E(t)$. We now imagine that we subject the rod to a cyclic strain

$$\varepsilon(t) = \varepsilon_0 \exp(i\omega t).$$

According to the Boltzmann superposition principle, the stress is

$$\sigma(t) = \int_{-\infty}^t E(t-u) \frac{d\varepsilon}{du} du = i\omega\varepsilon_0 \int_{-\infty}^t E(t-u) \exp(i\omega u) du.$$

Change the variable, $v = t - u$, and we obtain that

$$\sigma(t) = i\omega\varepsilon_0 \exp(i\omega t) \int_0^{\infty} E(v) \exp(-i\omega v) dv.$$

Consequently, the complex modulus is

$$E^*(\omega) = i\omega \int_0^{\infty} E(v) \exp(-i\omega v) dv.$$

Thus, the complex modulus relates to the relaxation modulus by the Fourier transform. The complex compliance is similarly related to the creep compliance. Recall that $E^*(\omega) = 1/D^*(\omega)$.

Consequently, all these moduli and compliances can be converted from one to another. They contain equivalent information.

10. Multiaxial stress state

When a solid is subject to a history of multiaxial stress, $\sigma_{ij}(t)$, the history of strain is

$$\varepsilon_{ij}(t) = \int_{-\infty}^t D_{ijpq}(t-s) \frac{\partial \sigma_{pq}}{\partial s} ds,$$

where $D_{ijpq}(t)$ is the tensor of creep compliance.

11. Example: Plane waves in a viscoelastic solid.

Viscoelasticity introduces a time scale into the problem, so that the waves must be dispersive. Here we limit our analysis to waves with a sinusoidal profile. To illustrate essential features, we will consider waves propagating in a rod.

First let us list the governing equations on the basis of the three ingredients of solid mechanics. The balance of momentum requires that

$$\frac{\partial \sigma}{\partial x} = \rho \frac{\partial^2 u}{\partial t^2}.$$

The strain-displacement equation is

$$\varepsilon = \frac{\partial u}{\partial x}.$$

These two ingredients are independent of the material. The third ingredient, the material law, will invoke visco-elasticity.

We will use complex numbers:

$$u(x, t) = u^*(x, \omega) \exp(i\omega t)$$

$$\varepsilon(x, t) = \varepsilon^*(x, \omega) \exp(i\omega t)$$

$$\sigma(x, t) = \sigma^*(x, \omega) \exp(i\omega t).$$

Using the complex amplitudes, the three ingredients of solid mechanics are written as follows. The balance of momentum now requires that

$$\frac{\partial \sigma^*}{\partial x} = -\rho \omega^2 u^*$$

The strain-displacement equation now becomes

$$\epsilon^* = \frac{\partial u^*}{\partial x}$$

The materials law is

$$\sigma^* = E^*(\omega) \epsilon^*$$

A combination of the three ingredients gives that

$$E^* \frac{\partial^2 u^*}{\partial x^2} + \rho \omega^2 u^* = 0.$$

The solution is

$$u^*(x, \omega) = A \exp\left(-i \sqrt{\frac{\rho}{E^*}} \omega x\right) + B \exp\left(i \sqrt{\frac{\rho}{E^*}} \omega x\right).$$

A wave propagating in the positive direction of x takes the form

$$u(x, t) = A \exp\left(-i \sqrt{\frac{\rho}{E^*}} \omega x + i \omega t\right).$$

Write

$$E^* = E_0 \exp(i\delta).$$

The above solution becomes

$$\begin{aligned}
 u(x,t) &= A \exp \left(-i \sqrt{\frac{\rho}{E_0}} \exp \left(-i \frac{\delta}{2} \right) \omega x + i \omega t \right) \\
 &= A \exp \left(-\sqrt{\frac{\rho}{E_0}} \omega \sin \left(\frac{\delta}{2} \right) x \right) \exp \left(-i \sqrt{\frac{\rho}{E_0}} \omega \cos \left(\frac{\delta}{2} \right) x + i \omega t \right)
 \end{aligned}$$

The wave propagates at the velocity

$$c = \sqrt{\frac{E_0}{\rho}} \sec \left(\frac{\delta}{2} \right).$$

The amplitude of wave decays exponentially as it propagates. The decay length is

$$l = \frac{c}{\omega \tan(\delta/2)}.$$

This concludes our brief introduction of viscoelasticity. The book by Ferry contains descriptions of experiments and data. The book by Christensen contains many solved boundary value problems. AQAQUS can be used to solve viscoelastic boundary value problems.