Linear response of materials: elastic, viscous, viscoelastic

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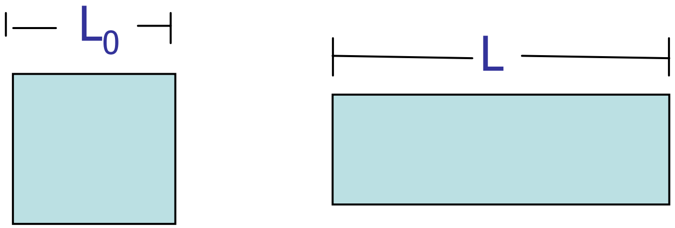
Elasticity. Linear elasticity

- Elasticity is a property of matter typical of the solid state. An elastic solid can be deformed by applying suitable forces, and recovers the original shape when those forces are removed.
- Locally, i.e. in a small neighborhood of a material point, elasticity is described by a relationship (a constitutive equation) that links stresses and strains at that point. Such a relationship is generally nonlinear.
- However, if only small strains (or small stresses) are considered, the relationship becomes linear.
- Said differently, when one starts deforming (or forcing) an elastic material, the initial response is always linear, to become nonlinear only eventually, when strains (or stresses) are large.
- We will only consider amorphous solids, like glass or rubber. Crystals are more complicated, because they are anisotropic, i.e., their response to deformation depends on how the crystal is oriented.
- As we have mentioned at the end of the first lecture, the elasticity of amorphous solids is described by a function that links the stress tensor **T** to some pure deformation tensor, e.g. **U**, or the quadratic Finger tensor **B**, measured from the stress-free, equilibrium state used as reference. Let’s now see what that function becomes in the limit of small deformations.

Small deformations in uniaxial extension

- We recall that we have introduced as a scalar measure of the extention, the stretch ratio $\lambda = L/L_0$



- If the deformation is small, i.e., λ is close to unity, it becomes convenient to introduce the strain ε :

$$\varepsilon = \lambda - 1 = (L-L_0)/L_0 << 1 \qquad (1)$$

- To achieve a (small) strain, a force per unit area is required, given by:

$$F/A = E\,\varepsilon \qquad (2)$$

  where the coefficient of this linear law is the Young's modulus.

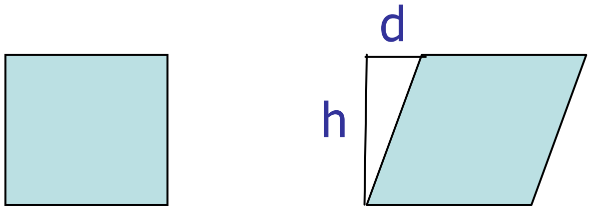
- If the extension occurs along x, the material element contracts along y and z. The corresponding strains are therefore negative, given by:

$$\varepsilon_y = \varepsilon_z = -\, m\,\varepsilon \qquad (3)$$

  where m is Poisson's ratio ($m \leq ½$). If the material is such that volume is preserved, then $m = ½$.

Small deformations in shear

- For this case, we require that $\gamma << 1$



Shear strain = γ = d/h

- For whatever amorphous material, a stress that generates a small shear strain does not modify the volume. The tangential stress σ is linked to γ by

$$\sigma = G\gamma \qquad (4)$$

where G is the shear modulus.

- Among the 3 material constants so far introduced (G, E, m) there exists a relationship, namely

$$E = 2G(1+m) \qquad (5)$$

- Thus linear elasticity of amorphous materials is characterized by 2 material constants only. For the important case of volume-preserving materials, since m=½ , Eq.(5) becomes

$$E = 3G \qquad (5')$$

and hence a single material constant, G or E, describes linear behavior.

Strain tensor

- Linear elasticity can be generalized to arbitrary small deformations.
- In order to do so, for an arbitrary deformation **E**, let us recall the pure deformation tensor **U** of Eq. (7) in Lecture 1, which has the canonical matrix

$$\|\mathrm{U}\| = \begin{vmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{vmatrix} \qquad (6)$$

  where the λ_i's are the principal stretch ratios of the deformation.
- Small deformations will generate λ values close to unity. In such a case, it becomes convenient to introduce differences from unity: $\varepsilon_i = \lambda_i - 1$, which are principal values of the strain tensor **V** = **U** – **I**. The matrix of **V** is then:

$$\|\mathrm{V}\| = \begin{vmatrix} \varepsilon_1 & 0 & 0 \\ 0 & \varepsilon_2 & 0 \\ 0 & 0 & \varepsilon_3 \end{vmatrix} \qquad (7)$$

- The sum of the ε_i's, i.e., the *trace* of **V** = tr**V** gives the fractional volume change $\Delta V/V$ due to (small) deformations. For volume preserving materials, we must have: tr**V** = 0.

Constitutive equation for linear elasticity

- The constitutive equation (C.E. in the following) of linear elasticity is, by definition, the most general equation linking linearly the stress tensor **T** to the strain tensor **V**. Assuming that the strain **V** is measured from the stress-free equilibrium configuration, we can write in general:

  $$\mathbf{T} = a\,\mathbf{V} + b\,\mathbf{I}\,\mathrm{tr}\mathbf{V} \tag{8}$$

  where a and b are 2 constants that characterize the specific material.
- It is more transparent, however, if we rewrite Eq. (8) as

  $$\mathbf{T} = 2G\,(\mathbf{V} - \mathbf{I}\,\mathrm{tr}\mathbf{V}/3) + K\,\mathbf{I}\,\mathrm{tr}\mathbf{V} \tag{9}$$

  where the two material constants are G, i.e., the shear modulus previously defined, and K, which is the bulk modulus.
- To understand Eq. (9), note that, since $\mathrm{tr}\mathbf{I} = 3$, the tensor in bracket $(\mathbf{V} - \mathbf{I}\,\mathrm{tr}\mathbf{V}/3)$ is traceless. Hence, the first term of Eq. (9) refers to a change in shape at constant volume (like the shear deformation), while the second term gives the isotropic stress due to a change in volume at constant shape.
- The relationship between G, K, m is: $K = (2/3)G(1+m)/(1-2m)$, showing that for m close to ½, the bulk modulus K is much larger than G, i.e., stresses that are sufficient to change the shape are not able to change the volume of the material.
- For volume-preserving materials, $\mathrm{tr}\mathbf{V} = 0$. Hence Eq. (9) becomes: $\mathbf{T} = 2G\,\mathbf{V}$.

The measure of small strains is essentially unique

- Assume that, instead of **U**, one wants to measure pure deformations with the Finger tensor $\mathbf{B} = \mathbf{U}^2$ which, we recall, is more readily calculated.
- The principal values of **B** are λ_i^2. For small deformations, these can be written as: $\lambda_i^2 = (1 + \varepsilon_i)^2 \cong 1 + 2\varepsilon_i$
- Hence, if we define the new strain measure:

  $$\mathbf{C} = \mathbf{B} - \mathbf{I} \qquad (10)$$

  we obtain, for small strains, the simple relationship:

  $$\mathbf{C} = 2\,\mathbf{V} \qquad (11)$$

  and the linear C.E. is readily rewritten in terms of the strain tensor **C.**
- This result is general in the sense that, for all possible pure deformation tensors, the corresponding small strain tensors are simply proportional to one another.
- For incompressible materials (like rubber), by using the strain tensor **C** defined in (10), the C.E. of linear elasticity becomes:

  $$\mathbf{T} = G\,\mathbf{C} \qquad (12)$$

  where G is the shear modulus.

Linear viscous (or Newtonian) response of fluids

- Most fluids are isotropic at equilibrium. But liquid crystals are an important exception (not considered here).
- In isotropic fluids undergoing flow, on top of the isotropic pressure a viscous stress tensor **T** arises, which is expected to depend on the strain rate tensor **D**.
- Similarly to Eq. (9), the most general linear law relating **T** to **D** is:

  $$\mathbf{T} = 2\eta\,(\mathbf{D} - \mathbf{I}\,\mathrm{tr}\mathbf{D}/3) + \eta_b\mathbf{I}\,\mathrm{tr}\mathbf{D} \tag{13}$$

  where η is the shear viscosity, and η_b the bulk viscosity.
- Indeed, $\mathrm{tr}\mathbf{D} = \partial v_x/\partial x + \partial v_y/\partial y + \partial v_z/\partial z = \nabla\cdot\mathbf{v}$ is the divergence of the velocity field, coinciding with the rate of dilation of the volume element.
- Most liquids can be taken as incompressible, i.e., $\mathrm{tr}\mathbf{D} = 0$ for them; hence

  $$\mathbf{T} = 2\eta\,\mathbf{D} \tag{14}$$

  is the simple C.E. of Newtonian liquids.
- Newtonian behavior is observed at small strain rates (said differently, in slow flows). Since the strain rate has dimensions of inverse time, being “small” implies comparison with some other “rate” intrinsic to the material. We postpone further discussion of this important point.

Linear viscoelasticity

- Many materials, especially polymeric ones, exhibit both elastic and viscous behavior. They are called viscoelastic. There exist viscoelastic solids and viscoelastic liquids, though sometimes the distinction can be difficult.
- To approach viscoelasticity, specifically linear viscoelasticity, let us start from the case of solids. These, when perfectly elastic, obey Eq. (9) in the general case, or Eq. (12) if incompressible. The crucial difference introduced by viscoelasticity is that the moduli G and K become time dependent.
- Limiting our discussion to the incompressible case, Eq. (12) becomes

  $$\mathbf{T}(t) = G(t)\,\mathbf{C} \qquad (15)$$

  with the following meaning: At time t=0 a small strain **C** is applied to the material element, and the strain **C** is held constant therefrom. A stress immediately arises like in purely elastic solid: $\mathbf{T}(0) = G(0)\,\mathbf{C}$. Subsequently, however, the stress decays in time.
- The material function G(t) is called relaxation (shear) modulus, and is always a decreasing function of time.
- The experiment to which Eq. (15) applies is called: stress relaxation after a step strain.

Viscoelastic solids vs. viscoelastic liquids

- The relaxation process just described is irreversible, and dissipates at least part of the work done initially to deform the material element. To the dissipation accompanying a deformation we associate the word “viscous”. Therefore, materials obeying Eq. (15) in step strain are called viscoelastic.
- If the viscoelastic material to which Eq. (15) applies is a solid, then G(t) in the course of time approaches a nonzero value, G_∞. That is, although stress decreases in time during relaxation, it will approach a value which then stays on forever as long as the configuration corresponding to the strain **C** is maintained. The difference with respect to a perfectly elastic solid is that, for the viscoelastic case, the equilibrium stress associated to the strain **C** is smaller than the initial stress **T**(0).
- Eq. (15) applies to viscoelastic liquids as well. For such a case, however, G(t) decreases down to zero. Then, although the strain **C** is held constant, in due time the stress **T** vanishes entirely, the liquid material relaxing back to the isotropic equilibrium state. The work done initially is totally lost, and deformation is not recovered when the constraint imposing **C** is removed.
- As shown next, though introduced for the particular case of a step strain, the material function G(t) fully characterizes the linear viscoelastic response of incompressible materials.

Continuous deformation

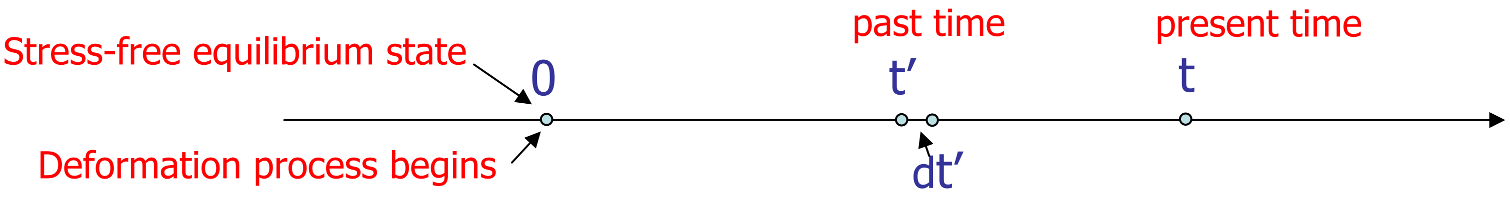
- For sake of simplicity, let us limit our presentation to a shear deformation, for which we can describe the strain tensor through the single scalar quantity γ (the shear strain), and the stress tensor through the tangential stress σ. (In the linear limit, normal stress differences are negligibly small.) For this case, Eq. (15) reduces to:

$$\sigma(t) = G(t)\,\gamma \qquad (15')$$

- Let us now assume that, starting at t=0 from the stress-free equilibrium configuration taken as reference, we deform the material element progressively in time. Such a process can be described through the function $\gamma(t)$, which gives the shear strain at time t. For solids, we assume that γ remains small at all times. For liquids, we temporarily make the same assumption.
- Our problem is finding the stress σ at time t, given the fact that we know the relaxation modulus G(t) of the material.
- The problem is that, while the strain is being augmented in time, thus generating additional stress, the stress due to previous strains is simultaneously relaxing.
- The strain increment is given by $\dot{\gamma}(t)dt$, where $\dot{\gamma}(t)$ is the shear rate at time t.

Boltzmann superposition principle

- Let us indicate with t′ any instant of time prior to present time t, when we want to know the stress $\sigma(t)$.



Stress-free equilibrium state

Deformation process begins

past time

present time

- The increment in strain between t′ and t′ + dt′ in the past is given by $\dot{\gamma}(t')dt'$. Such a differential strain step has generated a differential stress $d\sigma$ which, however, during the time interval between t′ and t has relaxed somewhat, obeying the relaxation rule given by Eq. (15′). Then, at the present time t, we expect that $d\sigma$ has become:

$$d\sigma(t) = G(t-t')\,\dot{\gamma}(t')\,dt'$$

- In view of linearity, we are entitled to sum over all such past contributions to the present stress (Boltzmann superposition principle). Hence:

$$\sigma(t) = \int_0^t G(t-t')\,\dot{\gamma}(t')\,dt' \tag{16}$$

C.E. of linear viscoelasticity

- Eq. (16) is the C.E. of linear viscoelasticity for incompressible materials (limited to shear deformations for simplicity). However, other forms can be derived from it that are useful too.
- Integration by parts transforms Eq. (16) into:

$$\sigma(t) = G(0)\,\gamma(t) - \int_0^t \mu(t-t')\,\gamma(t')\,dt' \qquad (17)$$

where

$$\mu(t) = -\,dG(t)/dt \qquad (18)$$

is called the memory function. Since G(t) <u>decreases</u> from G(0) towards either G_∞ (solids) or zero (liquids), $\mu(t)$ is always <u>positive</u>, and vanishes asymptotically as time goes to infinity for both solids and liquids, typically as a negative exponential of time (<u>fading memory</u>).

- Eq. (17) can be further manipulated to become:

$$\sigma(t) = G(t)\,\gamma(t) + \int_0^t \mu(t-t')\,\gamma(t,t')\,dt' \qquad (19)$$

C.E. of linear viscoelasticity (continued)

- In the last equation, $\gamma(t, t') = \gamma(t) - \gamma(t')$ is the strain at t relative to the configuration at t′, and is therefore independent of the reference configuration used to define $\gamma(t)$.
- Now consider the case where the time $t = 0$ (i.e., the time when we have started deforming the material) is so distant in the past that, at the present time t, the relaxation modulus G(t) has reached (exponentially fast) the asymptotic value G_∞ (for solids) or zero (for liquids). Eq. (19) can then be rewritten as:

Solids: $$\sigma(t) = G_\infty \gamma(t) + \int_{-\infty}^{t} \mu(t-t') \gamma(t, t') \, dt' \qquad (20)$$

Liquids: $$\sigma(t) = \int_{-\infty}^{t} \mu(t-t') \gamma(t, t') \, dt' \qquad (21)$$

where the lower limit of the integration has been formally changed from 0 to $-\infty$. Indeed, since G(t) has reached the asymptotic value at time t, also $\mu(t-t')$ is effectively zero for all negative values of t′, and the formal change makes no difference.

C.E. of linear viscoelasticity (concluded)

- Eqs. (20) and (21) remain valid also if time t = 0 is not so far back in the past to allow for the previous argument to be invoked. Indeed, as Eq.(19) was obtained by taking the material at t = 0 to be stress free, with no loss of generality we can imagine that at all previous times the element had never been deformed. Hence, we displace backwards the origin of time so as to fulfill the condition of the previous argument. Mathematically, the "trick" subtracts from the term outside of the integral in Eq. (19) (since G(t) is replaced by the smaller value G_∞ or 0) in favor of the integral itself, the lower limit of integration now being <u>effectively</u> lowered from 0 to $-\infty$.
- Therefore, Eqs (20) and (21) provide an alternative form of the C.E. of linear viscoelasticity for solids and liquids, respectively.
- By similar arguments Eq. (16) can be rewritten as:

Solids: $$\sigma(t) = G_\infty \gamma(t) + \int_{-\infty}^{t} \{G(t-t') - G_\infty\} \dot{\gamma}(t')\, dt' \qquad (22)$$

Liquids: $$\sigma(t) = \int_{-\infty}^{t} G(t-t') \dot{\gamma}(t')\, dt' \qquad (23)$$

Viscosity of a viscoelastic liquid in slow flows

- The linear equations of viscoelasticity were obtained under the condition that the strain $\gamma(t)$ remains small. While such a condition is mandatory for the case of solids, it is not so for liquids.
- Eq. (21) only contains relative strains $\gamma(t, t') = \gamma(t) - \gamma(t')$. Thus $\gamma(t)$ can grow indefinitely (as it certainly does in a steady shear flow) as long as the difference $\gamma(t, t')$ remains small for all values of t' where the memory function $\mu(t\text{-}t')$ gives non-negligible contribution to the integral.
- In other words, Eq. (21) (and 23) also applies to flows for which the deformation grows without bounds provided they are sufficiently slow, so that the memory of large deformations is lost, and only small, more recent, relative strains contribute to the current stress.
- In a steady shear flow, shear rate and shear stress are constant. Eq. (23) then becomes:

$$\sigma = \dot{\gamma} \int_{-\infty}^{t} G(t-t')\, dt' = \dot{\gamma} \int_{0}^{\infty} G(t)\, dt \qquad (24)$$

Hence the viscosity is the integral over time of the relaxation modulus:

$$\eta = \int_{0}^{\infty} G(t)\, dt \qquad (25)$$

Relaxation time

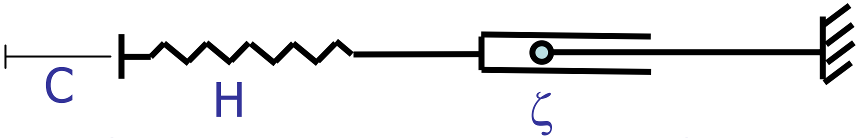
- We have seen that linear viscoelasticity of amorphous incompressible materials is fully characterized by a single material function, i.e. G(t), generating by differentiation the memory function μ(t). (Strains other than shear are readily considered by generalizing the previous C.E. to a tensor form.)
- Since μ(t) decays to zero, it is implicit in this function the concept of a "duration" of the memory, longer or shorter depending on the specific material as well as on other parameters, prominently temperature.
- Such a duration of the memory can be made explicit by defining a relaxation time τ of the viscoelastic material in the specified conditions.
- The definition of relaxation time is not unique, however, as any of the following ratios of moments of μ(t) can be used, or combinations of them, differing one from another by a numerical factor that depends on μ(t).
- We will see later that most materials exhibit a spectrum of relaxation times.
- If τ is immeasurably small, the material no longer is viscoelastic. It is either a viscous liquid or a perfectly elastic solid.

$$\tau = \frac{\int_0^\infty t^{n+1}\mu(t)dt}{\int_0^\infty t^{n}\mu(t)dt}$$

$$n > 0$$

A simple example: the Maxwell model

- Consider the mechanical model made up of a spring-and-dashpot device:



- The elastic constant of the spring is H, while the friction coefficient of the dashpot is ζ.
- Starting from the stress-free state, we apply a step displacement C.
- If x(t) is the spring elongation at time t, we then have $x = C$ at $t = 0$.
- Next, the spring relaxes by pulling over the dashpot. Balance of forces requires that: $H\,x = -\,\zeta\,dx/dt$
- We note that ζ/H has dimensions of time, and indicate such a ratio as τ.
- Balance is rewritten as $dx/x = -\,dt/\tau$, which integrates to $x = C \exp(-t/\tau)$.
- The relaxing force F(t) in the spring-dashpot device is then obtained as:

$$F(t) = H \exp(-t/\tau)\, C$$

- Comparison with Eq. (15) for step strain relaxation shows that the Maxwell model is equivalent to a viscoelastic liquid with the modulus:

$$G(t) = G \exp(-t/\tau) \qquad (26)$$

  where G is G(0), and relaxation occurs with a single relaxation time τ.
- From Eq. (25), the viscosity of a Maxwell liquid is given by: $\eta = G\tau$.

Frequency response (liquids)

- Suppose that the shear deformation is made to obey:

  $$\gamma(t) \;=\; \gamma_0 \sin(\omega t) \qquad (27)$$

  Here ω is the angular frequency of the oscillation, and γ_0 is the oscillation amplitude, which needs to be small if we want to stay linear.
- A nice aspect of the oscillatory experiment, also called "dynamic", is that it can be performed for solids and liquids alike.
- For liquids, to find the stress at time t, we apply Eq. (23). We obtain:

  $$\sigma(t) \;=\; \gamma_0\, \omega \int_{-\infty}^{t} G(t-t')\cos(\omega t')\, dt' \qquad (28)$$

- Changing integration variable to s = t-t', Eq. (27) becomes:

  $$\sigma(t)/\gamma_0 = \sin(\omega t)\{\omega\int_0^{\infty} G(s)\sin(\omega s)ds\} + \cos(\omega t)\{\omega\int_0^{\infty} G(s)\cos(\omega s)ds\} \qquad (29)$$

- Hence, the stress splits into a sin(ωt) part, in phase with γ, and a cos(ωt) one, out of phase with γ, and in phase with the strain rate. The respective coefficients are:

  liquids: $$G'(\omega) = \omega\int_0^{\infty} G(t)\sin(\omega t)dt; \quad G''(\omega) = \omega\int_0^{\infty} G(t)\cos(\omega t)dt \qquad (30)$$

Frequency response (solids)

- G′ and G″ are called storage modulus and loss modulus, respectively, or dynamic moduli, collectively.
- The in-phase and out-of-phase split

$$\sigma/\gamma_0 = G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t) \qquad (31)$$

  is of general validity for viscoelastic materials, liquids or solids, but the expressions for G′ and G″ in Eq. (30) apply to liquids only.
- For solids, from Eq. (22) we obtain:

solids:

$$G'(\omega) = G_\infty + \omega \int_0^\infty \{G(t) - G_\infty\}\sin(\omega t)\,dt$$

$$G''(\omega) = \omega \int_0^\infty \{G(t) - G_\infty\}\cos(\omega t)dt \qquad (32)$$

- Eq. (31) can be rewritten in terms of the complex modulus G* defined as

$$G^* = G' + i\,G'' \qquad (33)$$

  Eq. (31) then becomes (Re$\{\cdot\}$ means "real part of"):

$$\sigma/\gamma_0 = \mathrm{Re}\{-iG^*\exp(i\omega t)\} \qquad (34)$$

- Using the modulus of G*, and the phase φ, Eqs. (31) or (34) become:

$$\sigma/\gamma_0 = |G^*|\sin(\omega t + \varphi)\;; \qquad \tan\varphi = G''/G' \qquad (35)$$

Low frequency behavior

- In the integrals of Eqs. (30) and (32) (for liquids and solids, respectively), provided ω is small enough, $\sin(\omega t)$ and $\cos(\omega t)$ can be expanded around time $t = 0$, to become:

$$\sin(\omega t) \cong \omega t \qquad ; \qquad \cos(\omega t) \cong 1$$

- We then obtain:

liquids: $$G'(\omega) = \omega^2 \int_0^\infty t\, G(t)dt; \quad G''(\omega) = \omega \int_0^\infty G(t)dt = \eta\, \omega \qquad (36)$$

where we have used Eq.(25) for the viscosity η. Hence, in the limit of low frequencies, viscoelastic liquids show a storage modulus quadratic in ω, and a loss modulus proportional to ω through the viscosity η.

solids: $$G'(\omega) = G_\infty \quad ; \quad G''(\omega) = \omega \int_0^\infty \{G(t) - G_\infty\}dt \qquad (37)$$

In the low-frequency limit, viscoelastic solids show a constant storage modulus, and a loss modulus proportional to ω.

- The first integral appearing in Eq. (36) is encountered again in the creep experiment, through the so called steady-state compliance $J_e^{(0)}$, which is:

$$J_e^{(0)} = (1/\eta^2) \int_0^\infty t\, G(t)dt \qquad (38)$$

Dynamic moduli from the Maxwell model

- We now explicitly calculate the dynamic moduli for the Maxwell model of a viscoelastic liquid (single relaxation time).
- It is convenient to use complex number notation. From the definition of G*, Eq. (33), the result we obtained for liquids, Eq. (30), becomes:

$$G^* = i\omega \int_0^\infty G(t) \exp(-i\omega t)\, dt \qquad (30')$$

- For the Maxwell model G(t) is given by Eq. (26); hence:

$$G^* = i\omega G \int_0^\infty \exp(-t/\tau - i\omega t) dt = G\, i\omega\tau \int_0^\infty \exp(-x) dx/(1+i\omega\tau) = G\, i\omega\tau/(1+i\omega\tau) \qquad (39)$$

- Real and imaginary parts of G* then give:

Maxwell model:

$$G'(\omega) = G\, \omega^2\tau^2/(1+ \omega^2\tau^2)$$

$$G''(\omega) = G\, \omega\tau/(1+ \omega^2\tau^2) \qquad (40)$$

Frequency response of the Maxwell model

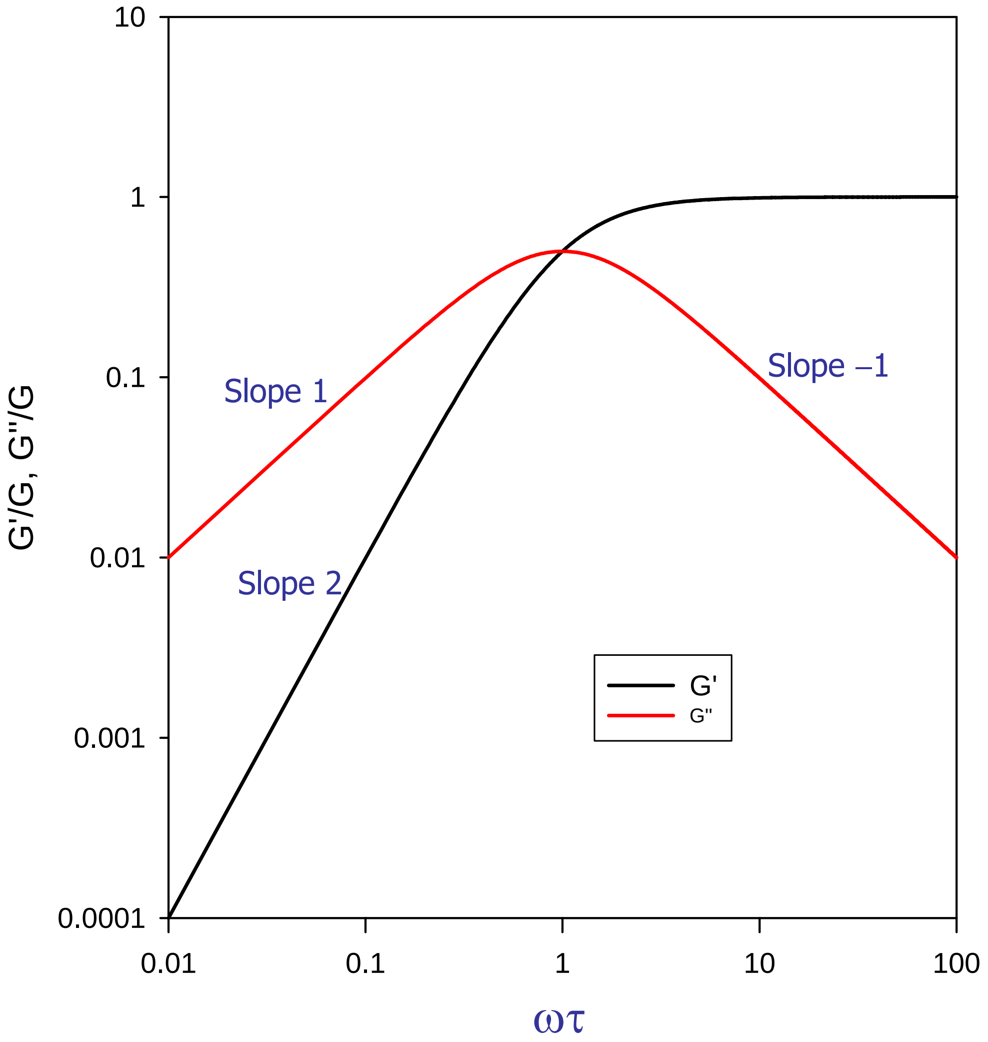
At high frequencies, G′ approaches a plateau value (here = G)

G″ shows a maximum at $\omega = 1/\tau$

The two curves cross at $\omega = 1/\tau$

At crossing G′ = G″ = G/2

The frequency response of many viscoelastic liquids departs, more or less significantly, from that of the Maxwell model, due to a spectrum of relaxation times. The basic features of this model, however, remain useful to understand more complex cases.



Complex viscosity

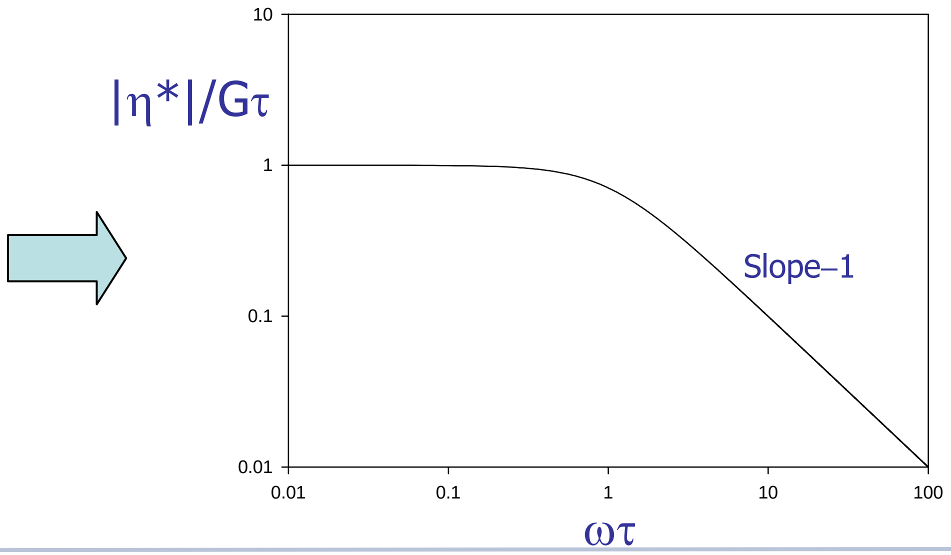
- The frequency response of viscoelastic liquids is often expressed in terms of a complex viscosity η^*, instead of the complex modulus G*.
- The relationship between the two is:

$$\eta^* = -i\, G^*/\omega = G''/\omega - i\, G'/\omega = \eta' - i\,\eta'' \qquad (41)$$

- Hence, $\eta'=G''/\omega$ gives (to within $\gamma_0\omega$) the stress in phase with the shear rate, and $\eta''=G'/\omega$ that out-of-phase.
- For the Maxwell model, the modulus of η^* is calculated from Eq. (40) as:

$$|\eta^*| = G\tau/(1+\omega^2\tau^2)^{1/2} \qquad (42)$$

Complex viscosity of Maxwell model



Creep

- So far we have always considered experiments where a deformation is imposed, and the resulting stress is then measured.
- The opposite procedure is also possible, however, i.e. stress is imposed, and the resulting deformation is recorded.
- Previous equations of linear viscoelasticity can be inverted. For example, Eq.(23) would be inverted to

$$\gamma(t) = \int_{-\infty}^{t} J(t-t')\,\dot{\sigma}(t')\,dt' \qquad (43)$$

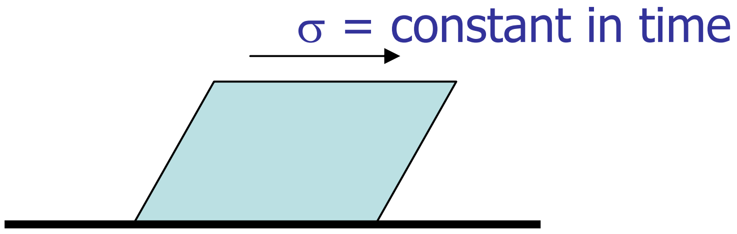
where $\dot{\sigma}(t)$ is the time derivative of the shear stress, and J(t) is a material function called creep compliance (dimensions of inverse modulus).

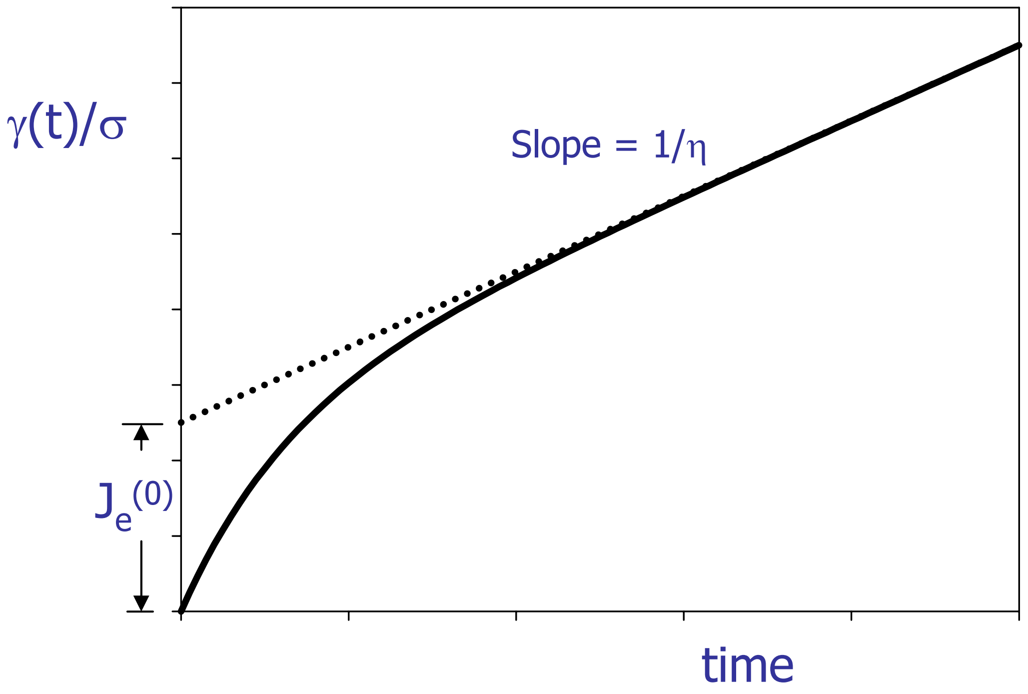
- In the creep experiment, starting from the stress-free equilibrium state, a (small) stress σ is suddenly applied, and kept constant thereafter. The resulting deformation γ is recorded as a function of time.
- In a viscoelastic liquid, $\gamma(t)$ keeps growing in time, asymptotically approaching a straight line, given by the equation:

$$\gamma(t)/\sigma = t/\eta + J_e^{(0)} \qquad (44)$$

where η is the viscosity, and $J_e^{(0)}$ is the steady-state compliance, previously introduced in Eq. (38).

The creep experiment





Relaxation spectrum

- The Maxwell model describes G(t) as a single negative exponential.
- More generally, G(t) (for solids $G(t) - G_\infty$) can be described as a sum of negative exponentials, each relaxation time τ_i generating a term with its own magnitude G_i at $t = 0$:

$$G(t) \;=\; \Sigma\, G_i \exp(-t/\tau_i) \qquad (45)$$

- Viscosity is then given by:

$$\eta \;=\; \Sigma\, G_i\tau_i \qquad (46)$$

- Similar sums are readily obtained for $G'(\omega)$, $G''(\omega)$, etc.
- From the discrete spectrum of relaxation times, we can move on to a continuous one. Instead of a discrete set $\{G_i, \tau_i\}$, a continuous spectrum is described by a function $H(\tau)$ (dimensions of a modulus) such that:

$$G(t) \;=\; \int_{-\infty}^{+\infty} H(\tau) \exp(-t/\tau)\, d\ln\tau \qquad (45')$$

- The viscosity is obtained as:

$$\eta \;=\; \int_{-\infty}^{+\infty} \tau\, H(\tau)\, d\ln\tau \qquad (46')$$