

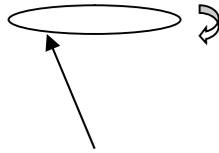
# Viscoelasticity

(with a comparison to light absorption: not as random as it may seem because there is just one physics)

*Introduction: bridging that gap between chemistry and tangible materials.*

Since we started a few days ago with morphology, we have been trying *not* to think like chemists or even molecular engineers. That is, we have taken off the molecular glasses. Now we are going to look at time-dependent perturbations of materials—a kind of mechanical spectroscopy. Since it's spectroscopy, let's put on the chemical glasses for a little bit and see what turns up.

Consider an NMR. The field precesses at a particular frequency (the Larmor



Precessing magnetic moment, comprised of zillions of small magnetic moments—e.g. on protons.

frequency) which is typically 500 MHz in a modern NMR instrument. To flip the field upside down we apply an electromagnetic (EM) field of the same frequency. Higher or lower frequencies don't work. (For you NMR junkies, I am thinking of a *continuous wave* instrument, not an FT NMR).

What is the mechanical analog? Let's consider a gyroscope, which similarly precesses in Earth gravity. To alter its orientation, we tap it with a hammer. What works well is applying the hammer at the same frequency. Too fast and the hammer doesn't spend enough time interacting with the gyroscope. Too slow and it never hits the gyroscope. Thus, the relationship between normal chemical spectroscopy and mechanical spectroscopy is established...kind of. We will now develop a more general formalism for beating up on physical objects, but we may expect to see some similarities to good old chemical spectroscopy. And we may learn something new about that, too.

## *Mechanical Spectroscopy*

We studied viscosity of liquids early in the course, introducing Newton's law for viscosity. We also saw Hooke's law in association with deGennes' development of  $\alpha^2$ . Here they are:

$\sigma = \eta \dot{\gamma}$		Liquid in shear	Eq. <1>
$F = k' \Delta x = k \Delta x / x$		Solid in extension	Eq. <2>

These two equations represent viscous liquids (in shear) and elastic solids (in extension). Remember that  $\sigma = F/A$  so apart from being normalized by area the first is really a force equation, as is the 2<sup>nd</sup>. Also remember that  $\gamma$  is a dimensionless deflection:

$$\gamma = \Delta x/y \quad \text{Eq. <3>}$$

so...

$$\dot{\gamma} = (1/y)\left(\frac{d\Delta x}{dt}\right) \quad \text{Eq. <4>}$$

Wow! This makes it clear that our two equations for force are totally different. Newton's law says that the force of viscosity is related to the *time derivative* of the deflection  $\Delta x$ . Hooke's law says that the force of stretching is related directly to  $\Delta x$  itself. This means the equations describe flat-out different phenomena. No big surprise, because it means that solids and liquids are just different things.

You can tell by the *sound* of them.

- Solids: *ping, click, bang* (e.g. a bell)
- Liquids: *slosh, flush, squish* (e.g. milk)

## Jello-O What's this stuff?

You can't hear Jell-o wiggling, but an elephant might. It vibrates at some low frequency like an elastic solid. Put some in a bowl and you can *feel* it wiggle. You will even find that well-aged jello vibrates at a higher frequency—more “ping”. Yet it doesn't wiggle for long; vibrations dampens away, as they would in a liquid, say honey. If we were to adopt that molecular view again, we would find that the water molecules move almost unimpeded through the gel...or the honey.

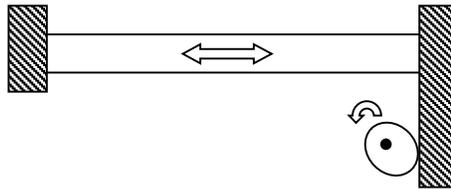
### *Generalizing the mechanical response of things*

Let's always write our forces as force per unit area—i.e., stress. In shear, “area” means the area of the contact plates; in compression or elongation it means the cross-sectional area normal to the applied force. By the way, there is such a thing as viscosity in extension (or compression). The easiest way to think of this is to remember that viscosity is not only the coefficient between stress and rate of strain; in that Einstein picture we developed, it is also a coefficient of energy loss. We continue to make strains dimensionless by dividing the displacement by some other length ( $y$  in shear;  $x$  in elongation). Then we can write:

$$\sigma_{elastic} = E_1\gamma \quad (\text{storage of energy}) \quad \text{Eq. <5>}$$

$$\sigma_{viscous} = E_2\dot{\gamma} \quad (\text{loss of energy}) \quad \text{Eq. <6>}$$

Note that  $E_1$  and  $E_2$  don't have the same units ( $E_1$  is Pa and  $E_2$  is Pa·s). Now imagine an experiment where the distortion of the object is applied sinusoidally. Let's say we have a 100 mm bar of plastic and we clamp it at either end in a device driven by a cam that can extend it by 1 mm in a sinusoidal fashion.



The strain ( $\Delta x/x$ ) follows

$$\gamma = \gamma_0 \sin(\omega t) \quad \text{Eq. <7>}$$

where  $\omega$  is the circular frequency (i.e.,  $2\pi\nu$  with  $\nu$  the actual frequency) and  $\gamma_0$  is the maximum strain amplitude (1% in the case imagined above). The cam and clamp assembly must exert a force per unit area of  $\sigma$  to achieve the strain  $\gamma$ . One might imagine a feedback loop, such that whatever stress is necessary will be provided to keep the strain to the prescribed sine form. Thus, both  $\sigma$  and  $\gamma$  are known as functions of time.

Now, here's the important part. The  $\sigma$  required to maintain the desired strain is the *sum* of the elastic and viscous terms.

$$\sigma_{sum} = \sigma_{elastic} + \sigma_{viscous} = E_1\gamma + E_2\dot{\gamma} = E_1\gamma_0 \sin(\omega t) + E_2\omega\gamma_0 \cos(\omega t) \quad \text{Eq. <8>}$$

This is neat! The total stress is partly due to the sine term and partly due to the cosine term. So, now we need to understand how weighted sums of cosines and sines behave. That's a good project for Excel, and you should now download a spreadsheet we designed to look at what happens (TanDelta.XLS in the "downloads" section).

The results of fiddling with this Excel spreadsheet are:

*A weighted sum of sine and cosine waves also oscillates with frequency  $\omega$  but with a different phase, which depends on the relative magnitude of  $E_1$  and  $E_2$ .*

In equation form, our Excel observations are consistent with the summed stress obeying:

$$\sigma_{sum} = E\gamma_0 \sin(\omega t + \delta) \quad \text{Eq. <9>}$$

where  $E$  (no subscript) is "some modulus" and  $\delta$  is the phase lag from the original sinewave.

The phase lag  $\delta$  is a good indicator of the strength of the loss modulus  $\omega E_2$  compared to the storage modulus,  $E_1$ . When  $\omega E_2 \ll E_1$  (elastic solids) then  $\delta = 0$ . When

$\omega E_2 = E_1$  then  $\delta = 45^\circ$ . When  $\omega E_2 \gg E_1$  (viscous liquids) then  $\delta = 90^\circ$ . We can pursue this further by rewriting the previous equation, taking advantage of the sine sum rule:

$$\sigma_{sum} = E\gamma_o \sin(\omega t) \cos(\delta) + E\gamma_o \cos(\omega t) \sin(\delta) \quad \text{Eq. <10>}$$

Comparing this to Eq. <8> reveals the relationship between  $E_1$  and  $E_2$  and the “some modulus”  $E$ .

$$\begin{aligned} E_1 &= E \cos(\delta) \\ \omega E_2 &= E \sin(\delta) \end{aligned} \quad \text{Eq. <11>}$$

$$\frac{\sin(\delta)}{\cos(\delta)} = \tan(\delta) = \frac{\omega E_2}{E_1} \quad \text{Eq. <12>}$$

Consistent with our Excel observations, this produces  $\delta = 45^\circ$  when  $\omega E_2 = E_1$ . No one actually uses  $\delta$ , though. The commonly reported parameter is actually  $\tan(\delta)$ . Note that the liquid state (more correctly, the dominance of viscous response over elastic) corresponds to  $\tan(\delta) = \infty$ . The elastic limit corresponds to  $\tan(\delta) = 0$ .

<b>tan(δ)</b>	<b>Physical meaning</b>
0	Elastic limit
1	Balance
∞	Viscous limit

**Other symbols.** For shear experiments, one often uses  $G$  instead of  $E$ . Also, it is common to use primes instead of subscripts. For example,  $G'$  is a shear storage modulus and  $G''$  is a shear loss modulus.

### Complex Notation

Somewhere in your past, you should have encountered complex notation, complex variables, etc. in which we use the imaginary numbers like  $i = \sqrt{-1}$ . This greatly simplifies the discussion of periodic phenomena. If you haven't revisited the Argand diagram in a while, you might wish to. If you never heard of it, try the internet! With complex notation, we can just write:

$$\begin{aligned} \gamma &= \gamma_o e^{i\omega t} \\ \sigma &= \sigma_o e^{i(\omega t + \delta)} \end{aligned} \quad \text{Eq. <13>}$$

Now we can define a complex modulus,  $E^*$ :

$$E^* = \frac{\sigma}{\gamma} = \frac{\sigma_o e^{i(\omega t + \delta)}}{\gamma_o e^{i\omega t}} = \frac{\sigma_o}{\gamma_o} e^{i\delta} \quad \text{Eq. <14>}$$

But from our general knowledge of complex numbers, we know that:

$$e^{iz} = \cos(z) + i \sin(z) \quad (\text{where } z \text{ is anything}). \quad \text{Eq. <15>}$$

Thus,

$$E^* = \frac{\sigma_o}{\gamma_o} (\cos \delta + i \sin \delta) \quad \text{Eq. <16>}$$

This is just:

$$E^* = E_1 + iE_2 \quad \text{Eq. <17>}$$

What this shows is: our separate concepts of storage modulus and loss modulus are unified in a single *complex* modulus! The storage is the real part of the complex modulus and the loss is the complex part. The , the units are the same...Pascals (Pa).

### *Denouement*

This story began with a consideration of NMR spectra (could just as easily have been infrared). The point is that light is a way of beating up on molecules in the same way that mechanical devices are ways of deforming materials: in both cases, the problem is a driven, damped harmonic oscillator! Oh, sure...the absorption is best treated by quantum mechanical analogies of the driven, damped harmonic oscillator...but that is just a detail. We'll end with an analogy to optical systems to drive this home.

The electric field of light can be expressed as a travelling wave:

$$E_{light} = E_o e^{ikx} e^{i\omega t} \quad \text{Eq. <18>}$$

The time part ( $e^{i\omega t}$ ) takes care of the rapid oscillations. If you are standing still at some given point in space, the light field will oscillate as it races past you. The space part takes care of phase arguments: at a given instant of time, the field will be higher or lower depending on where you are, varying periodically over a distance  $\lambda$ . The variable  $k$  describes the *spatial* frequency of the light:

$$k = 2\pi/\lambda \quad \text{Eq. <19>}$$

Now, the wavelength of light is the *in vacuo* value, divided by the refractive index:

$$\lambda = \lambda_o/n \quad \text{Eq. <20>}$$

Thus:

$$k = 2\pi n/\lambda \quad \text{Eq. <21>}$$

OK, so that's the background--a quick recap of what you can see in any physics text. The most interesting things happen when you let  $n$  be a complex variable:

$$n^* = n + i\varepsilon \quad \text{Eq. <22>}$$

This leads naturally to:

$$k^* = \frac{2\pi}{\lambda}(n + i\varepsilon) \quad \text{Eq. <23>}$$

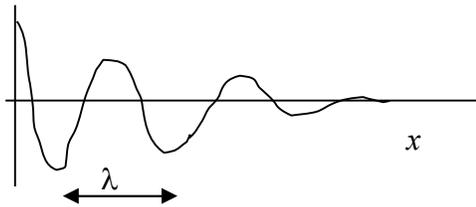
and:

$$E_{light} = E_o e^{\frac{2\pi}{\lambda}(n+i\varepsilon)x} e^{i\omega t} \quad \text{Eq. <24>}$$

We can expand out the spatial part, remembering that  $i^2 = -1$ :

$$E_{light} = E_o e^{\frac{2\pi}{\lambda}nx} e^{-\frac{2\pi\varepsilon x}{\lambda}} e^{i\omega t} \quad \text{Eq. <25>}$$

What does *this* say? As before, it says the electric field oscillates both in space and in time. But it also now *decays* in space!



That complex part of the refractive index is again the *loss* term. We chose a symbol  $\varepsilon$  for it in keeping with the usual chemical convention: it is related to the absorptivity. By analogy to our mechanical spectroscopy, we therefore see that the real part of the refractive index is elastic. Transparent media are those in which light energy propagates elastically so that energy is not lost. Absorptive media are “lossy”.

The analogy between mechanical and visible spectra should now be.....um....transparent, but that is not all. There are connections to electricity, too: resistors are lossy and capacitors elastic. Most real electrical networks are in-between—electrically viscoelastic? When you buy a capacitor, it comes with a  $\tan(\delta)$  specification!

http://www.datasheets360.com/part/detail/338lba035m2bc/-6511964411173125868?comp=6221

**Part #: 338LBA035M2BC**

Category: Capacitors  
Manufacturer: Illinois Capacitor, Inc.  
Description: CAPACITOR, ALUMINUM ELECTROLYTIC, NON SOLID, POLARIZED, 35 V, 3300 uF, THROUGH HOLE MOUNT



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**SPECIFICATIONS**

Mfr Package Description	ROHS COMPLIANT
Lead Free	Yes
EU RoHS Compliant	Yes
Status	ACTIVE
Terminal Finish	MATTE TIN
Mounting Feature	THROUGH HOLE MOUNT
Manufacturer Series	LBA
Operating Temperature-Max	85 Cel
Operating Temperature-Min	-40 Cel
Capacitance	3300 uF
Package Shape	CYLINDRICAL PACKAGE
Capacitor Type	NON SOLID
Terminal Shape	SNAP-IN
Negative Tolerance	20 %
Positive Tolerance	20 %
Rated DC Voltage (URdc)	35 V
ESR	125.6mohm
Polarity	POLARIZED
Tan Delta	0.25
Ripple Current	2.2A
Leakage Current	2310uA