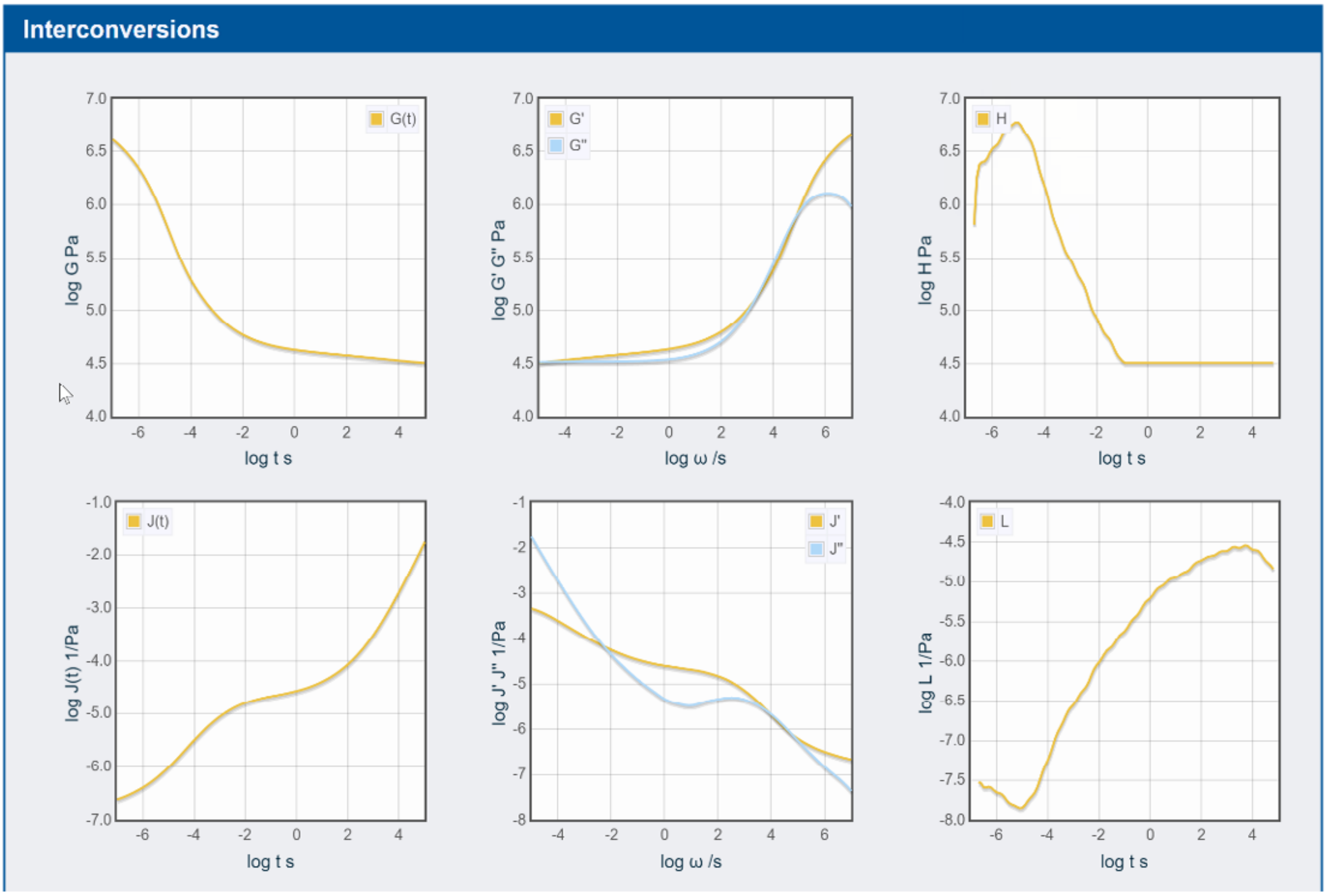
The Abbott Guide to Rheology



Prof Steven Abbott

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Version history:

First words written	7 November 2018
First draft issued	25 November 2018
Version 1.0.0	8 December 2018
Version 1.0.1	9 December 2018
Version 1.0.2	16 October 2019

Contents

Preface

"Maybe we should check out the rheology of this system" is the sort of sentence that can create panic and alarm in many people. Rheology has a reputation as being obscure and difficult, so people avoid it as much as possible. This is deeply unfortunate because, despite its bad reputation, rheology can deliver key insights to formulators and trouble-shooters and isn't, in fact, so difficult.

There are some excellent books on general rheology. I have especially valued Thomas Mezger's *Rheology Handbook* as he writes as an expert who knows his subject, his equipment and his audience well. This guide in no way wishes to compete with the 400pp of Mezger's book. There are also many excellent books on specific aspects of rheology such as Christopher Macosko's *Rheology Principles, Measurements and Applications* or Jan Mewis and Norman Wagner's *Colloidal Suspension Rheology,* from each of which I have learned a great deal. And the TA Instruments Webinar Series on YouTube is a great way to learn the details of rheological techniques from experts.

What is lacking in all these (precisely because they contain so much valuable information) is a stepping back from the detail to see rheology from the point of view of the harassed formulator who has an idea that rheology might be helpful but cannot see which measurements will help to solve a specific problem.

So this guide attempts to describe the problems we need to solve, along with the appropriate bit of rheology that helps provide the answers. In order to describe the problem we have to introduce some key ideas such as entanglement and relaxation times that are not at all hard but which are generally unknown or under-appreciated.

To make life easier for the reader and for myself (after all, I need to understand this stuff as well), I have written a set of apps on my Practical Rheology website, where you can see things live when they are discussed in this guide. Just click on the link to immediately start exploring. The apps are standard HTML5/ Javascrip/CSS3 so they run on phones, tablets and laptops, are safe on corporate networks, and are free and free of ads.

Along the way, the guide will point out why rheologists have created so much confusion for the rest of us, and, via apps, bring some order to that confusion. If any real rheologist reads this guide, maybe they will see the world through our non-expert eyes and try, in future, to be less confusing. I will also point out some huge flaws in the world of rheology. This is not to make fun of rheologists. The flaws are there because it is a genuinely difficult scientific challenge to fix them. If the flaws could be fixed then both rheology and the practical formulator would benefit strongly, for reasons I hope to make clear.

Because I am not a rheologist and have always struggled with rheology, I have had to rely on the wise input from a number of world-class rheology experts. I am especially grateful to one expert who, after glancing at an early prototype of Practical Rheology said "It's fine, except for the fact that you have omitted almost everything of importance". That assessment was entirely accurate and the resulting site is much improved from that crude prototype.

I would like to acknowledge my debt to, in alphabetical order, the experts:

- Prof Paul Bowen, Neil Cunningham, Seth Lindberg, Roelof Luth, Dr Hans-Martin Sauer, Dr Saeid Savarmand.

They have each helped me considerably, though I stress that all opinions and errors in the Guide are my own.

It was an automotive engineer from Germany, Sebastian Abbott, who mentioned how "Maybe we should check out the rheology of the system" seemed to induce panic. Rheology should be a routine methodology for those who need it as part of their day job, just as they need other measurements, such as spectra, in which they do not have to be great experts. It should not be a source of alarm. That quote was the inspiration for putting this guide together. The act of writing it has reduced my own sense of panic and alarm. I hope that it will do the same for you, the reader. Sebastian also provided a fine critique of a late draft of the guide. This prompted a significant rewrite and, I hope, a more user-friendly book.

Steven Abbott, Ipswich, 2018

1 Setting the scene

What problems are we trying to solve?

Your formulations can flow. At the very minimum you need some objective measure of the flow characteristics, and viscosity is the most basic method. Before worrying about what our viscosity should be, we need to be confident that we know what viscosity is.

A rather different problem is that talk of viscosity tends to include terms like stress and strain, and units like /s or Pa.s. We need to be confident about these too.

Rheology got off to a bad start for me thanks to two 6-letter words which in normal English mean the same and which start with the same 3 letters: stress and strain. As we cannot make the words go away we have to learn not to get confused.

1. **Stress** is a force per unit area applied to an object. Because force is in Newtons, stress is N/m^2 or Pa.
2. **Strain** is the % increase in length of an object when it is stressed; i.e. it is increase of length divided by the original length. It is a pure number, without units.

You can't get a strain without a stress and you don't have a stress without a strain. Rheologists seem to outsiders to make random decisions about the experiments they choose to do and the plots they present to us. This means that many experiments are done by imposing known stresses and measuring strains or, for no obvious reason, by imposing known strains and measuring stresses.

Rheological plots use Greek symbols so we have to get used to them, though unfortunately there is no consistency between rheologists. For stress I will use σ (others choose to use τ, which I will use as a timescale).

We are familiar with the expression for tensile modulus, stress over strain, usually shown as $E=\sigma/\varepsilon$. In rheology we usually use shear modulus (the resistance to strains across rather than along the sample) which is conventionally shown as G[1]. Because in rheology strain is usually shown as γ, we have the classic equation for the stress in a purely elastic material:

Equ. 1-1 $$\sigma = G\gamma$$

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[1] For a typical polymer, G=E/3, with the more precise conversion being G=E/2(1+v) where v is the Poisson ratio, typically 0.3-0.5.

As we shall see, most materials have a mixture of elastic and viscous properties so we need that equation later. For now we want to focus on viscosity, where I will try to use η consistently though you often see μ and I'm guilty of sometimes swapping accidentally between them.

For viscosity, strain is not useful because viscosity appears only when motion is involved. That is why we need strain *rate*, which is shown as γ with a dot above it, $\dot{\gamma}$, though my attempts to produce it always place the dot a bit lopsided. I find it very hard to spot whether people are discussing γ or $\dot{\gamma}$, another example of how rheologists have made our lives unnecessarily hard. Those who created the nomenclature knew that dot means "derivative" - without thinking through the implications for ordinary people who have to use their nomenclature.

Let us see how the idea of viscosity, strain rate and the required stress are inter-related.

We have all been taught to think of flow as a set of stream lines or, as in the diagram as little sheets of fluid sliding over each other. So let us think of the stress involved in trying to slide the top sheet at a velocity V with the velocity decreasing to the stationary bottom sheet over a distance Y.

Clearly we need more stress to move at a higher velocity. Less obviously, we need more stress when Y is smaller, because the drag of slower sheets on each sheet above is more extreme. So the stress required is proportional to V/Y. Because V is a velocity in m/s and Y is a distance in m, V/Y has the units of "per second", which can be shown as 1/s, /s or s^{-1}. They are all awkward[2] and I tend to use the first two, so you have to get used to seeing 1/s or /s appear in the text and on graphs in the apps. Technically V/Y is the "shear strain rate", i.e. the rate at which strain is created in shear, but we usually call it the shear rate and it is our $\dot{\gamma}$. We can write the standard (Newtonian) viscosity equation :

Equ. 1-2
$$\sigma = \eta\dot{\gamma}$$

which tells us that the stress required to shear a liquid is viscosity, η, times shear rate $\dot{\gamma}$. If you want to check out the calculation there is an app to do both the V/Y part and the stress part: https://www.stevenabbott.co.uk/practical-rheology/Viscosity-Basics.php.

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[2] When we come to Semi-Solids, my instinct was to write frequencies in Hz rather than /s. It seems more consistent to stay with /s and this also removes the question of whether we need to include a factor of 2π.

The equation also tells us that viscosity must have the units of stress/shear_rate, which is Pa/(1/s) giving us our viscosity unit of Pa.s. A viscosity of 1 Pa.s is quite high, so for convenience, lower viscosities are usually cited as cP, where 1 cP=1 mPa.s. It is annoying that we have P for Poise and Pa.s for Pascal seconds and many of us have messed up by mis-reading the unit and therefore being out by a factor of 10. So, look out for P (which is 0.1 Pa.s) and Pa.s and don't feel too bad if you occasionally get them confused.

And while we are talking about confusion we also have the rheology world usually talking in terms of "dynamic viscosity", η, while many fields involved with flow phenomena, especially gravitational flow, talk in terms of "kinematic viscosity" which is often shown as v (Greek nu) and is related via the fluid density ρ. Because v=η/ρ and because the density of most liquids isn't too far from 1, and because there are plenty of uncertainties in viscosity measurements, if I see a kinematic viscosity in cSt (centistokes) I just assume that it is a dynamic viscosity in cP.

Plots involving stress

Most of us think in terms of viscosity because we have a feel for what the numbers mean. For some reason, rheologists tend to think in terms of stress. So instead of plots of viscosity versus shear rate (with which we are all comfortable) we get plots of shear stress versus shear rate.

You just have to remember that you can derive viscosity from these plots simply by dividing the shear stress by shear rate. If the stress is 100Pa and the shear rate is 100/s then the viscosity is 100/100 = 1 Pa.s.

An alternative is to get used to seeing the many variations of plots that rheologists throw at us by playing with the app to be discussed shortly.

1.1 Never measure *a* viscosity

I was once troubleshooting on a production line. The science told me that their problem was the viscosity of their coating solution. I asked them what it was. They said it was 23s with a Zahn #2 cup. At the time I did not have my flow cup app (https://www.stevenabbott.co.uk/practical-rheology/Cup-Viscosity.php, though I do not recommend it and an expert rheologist was mad at me for writing it because it encourages people to continue with such barabaric measurements), so it took me some time to work out that this was ~70 cP. It also turns out that the measurement error of such a cup makes this 70±10, and eventually we found that anything above 75 cP (i.e. within their measurement accuracy) limited the process.

This is a typical example of how good people working on high-tech products are deeply unaware of how even basic rheology could transform their ability to control their product. With modest effort they could have found whether the viscosity was shear thinning (which would have helped) and how the viscosity changed with % solids. It turned out that, as is frequently the case, the solids had been pushed to a practical limit and that a small increase (via evaporation on the machine) leads to a significant increase in viscosity which in turn could create the coating defects I was there to troubleshoot. The common fact that a small change in polymer concentration can make a large difference to the viscosity is discussed later.

The first advice, therefore, is to never measure *a* viscosity and certainly to never use a flow cup. This is the 21st century and it is neither hard nor expensive to measure viscosities over a range of shear rates and over a relevant range of concentrations. Part of the reluctance to make such measurements is the perception that rheology is hard. I will make the case that rheologists make rheology unnecessarily hard, but rheology itself is not that difficult.

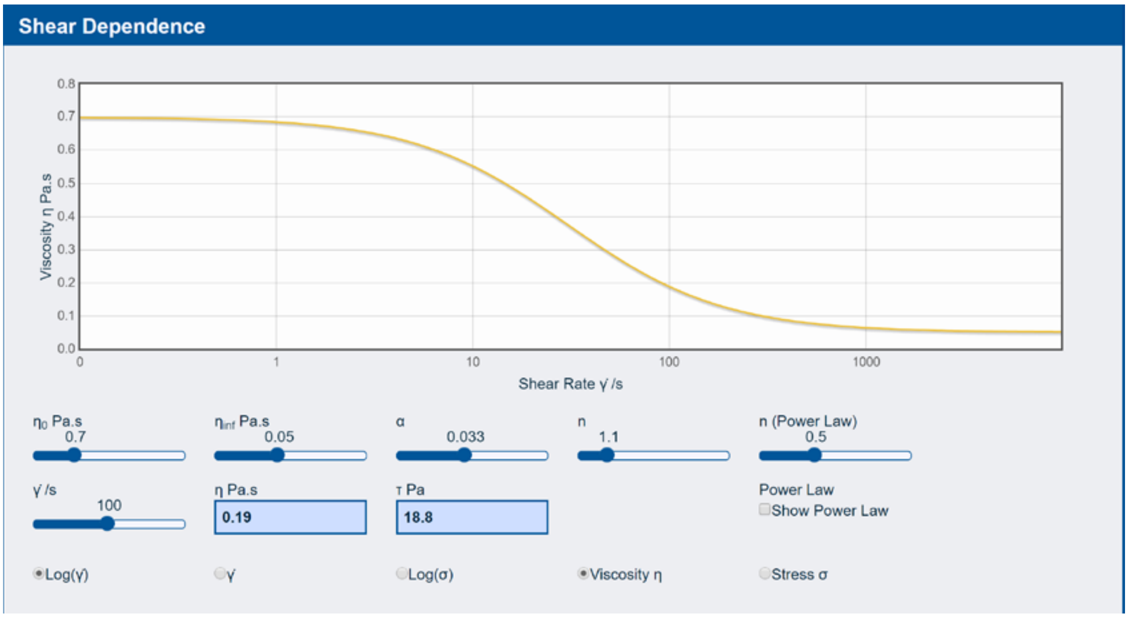
2 Shear-rate dependent viscosity

What problems are we trying to solve?

Giving our fluid a single "viscosity" usually is not good enough, so we need to know how the viscous behaviour changes with three important variables: shear rate, time and concentration.

The shear rate and time issues (shear thinning and thixotropy) are relatively familiar. Of more importance are the *reasons* for such behaviour and the *reasons* why we often find ourselves in a zone where small changes of concentration have a large effect on viscous behaviour. Once we understand the reasons (via entanglement and relaxation times) our ability to formulate around the problems is greatly enhanced.

As we all know, for many liquids viscosity changes with shear rate. Such liquids are called non-Newtonian. There are various equations to describe this dependence via some sort of curve fitting. I spent a pleasant hour reading papers indulging in major fights over the best form of curve fitting, but to the level of precision that most of us aspire to, good enough is good enough. Here is a typical graph of a how viscosity can change with shear rate:



η_0 Pa.s 0.7

η_{inf} Pa.s 0.05

α 0.033

n 1.1

n (Power Law) 0.5

$\dot{\gamma}$ /s 100

η Pa.s 0.19

τ Pa 18.8

Power Law

☐ Show Power Law

● Log($\dot{\gamma}$) ○ $\dot{\gamma}$ ○ Log(σ) ● Viscosity η ○ Stress σ

App 2-1 https://www.stevenabbott.co.uk/practical-rheology/Shear-Viscosity.php

It shows the viscosity behaviour over a wide range of shear rates and starts with a known low shear viscosity, η_0 and heads down to the limiting high shear viscosity, η_{inf}, via a parameter α which controls where the viscosity drop happens and n which controls how quickly it happens. This is all captured in the Cross equation, which happens to be my favourite:

Equ. 2-1 $$\eta = \eta_{\text{inf}} + \frac{\eta_0 - \eta_{\text{inf}}}{1 + (\alpha.\dot{\gamma})^n}$$

To be more precise about α, if the viscosity drops at 10/s then α = 0.1, i.e. 1/shear_rate. And when n = 0 the viscosity drops linearly from η_0 to η_{inf}, changing to a very sharp drop-off when n = 5. Whether you have *pseudoplastic* (shear thinning) or *dilational* (shear thickening) behaviour depends on whether the infinite shear viscosity is higher or lower than the zero shear value.

A key feature of the app is that in addition to providing the familiar view of viscosity behaviour, it models the many different ways the same behaviour is presented in the rheology literature. It is rather shocking to see how different the same data looks via different viewpoints.

Here are the same data plotted in four of the six different ways that the app can provide:

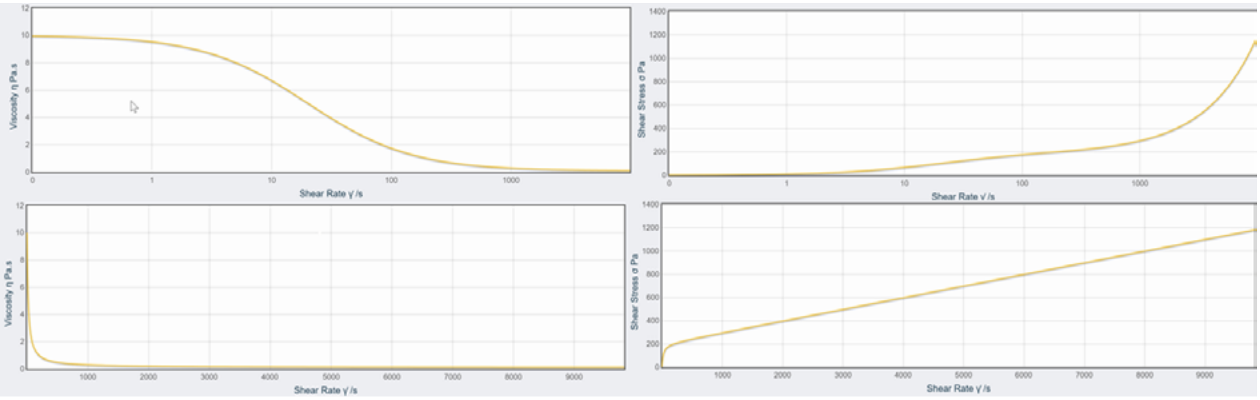


Figure 2-1 If you play with the app you will find that same data can look *very* different depending on what you choose to plot. On the left we have viscosity plots in log and linear modes and on the right, shear stress plots in log and linear.

The first shock is that for most of us, viscosity is constant over our range of interest - a fact that is obvious when we swap from a log to a linear plot as in the bottom left. The second shock is the top-right plot which is what many rheologists would instinctively plot - the stress versus shear rate. The bottom right plot is even stranger - there's some apparently irrelevant portion near the start then a strange steadily increasing stress. When you think about it, it is obvious what is going on: at the constant viscosity above a small shear rate, shear stress is proportional to shear rate. The problem with such plots is not so much that they are difficult but that it throws us when one system is discussed via, say, the top left plot while a similar system is discussed with the bottom right. Given that the overwhelming number of formulators are familiar only with the top left plot, maybe rheologists should choose this as their default.

The option to plot log(σ) along the X axis is one of the six plots because an especially famous set of curves related to shear thinning of particulate systems

uses this bizarre choice, and everyone just reproduces it rather than converting it to the rather similar standard log shear rate version. Each time rheologists throw us by showing a different plot, they weaken our will to use rheology.
If I look at an infra-red or NMR spectrum I can immediately look for the key information because all plots are done with a familiar set of rules. With rheology I first have to spend time worrying about what is being plotted before I can start looking at what the plot means. This is unacceptable.

For those who aren't bothered about what happens at very low shear rates, a power law model can be used. You can play with that option if you wish. Sometimes you need to do this if you are reading papers that focus on power laws (often for mathematical convenience) rather than Cross models, and want to get a feel for what is going on. The one discussed in the app is invoked by those who want to talk about the "P Ostwald" of their formulation, a crude description of its shear thinning behaviour.

Models at low shear rates

For low and super-low shear rates, models such as the Casson or the Herschel-Bulkley equation are often used, usually expressed in terms of stress. Here is Herschel-Bulkley in stress format:

Equ. 2-2 $$\sigma = \sigma_y + K\dot{\gamma}^n$$

It is easily translated into viscosity format:

Equ. 2-3 $$\eta = \frac{\sigma_y}{\dot{\gamma}} + K\dot{\gamma}^{(n-1)}$$

The dependence on shear rate via a power, n (typically ~0.5), means that these are power law models. If you stay in stress mode, the equations are well-behaved. The problem arises when you go into viscosity mode, which is generally what interests us, because it heads off to infinity at low shear rate.

We will return to these equations because σ_y is the Yield Stress which has a chapter all to itself.

2.1.1 Shear thinning and your process

At the start we defined the shear rate as V/Y, velocity over gap. So far in this chapter we have merely seen what happens to viscosities at different shear rates. We have made no attempt to apply that knowledge to a formulation. There is a very simple trick that can make you appear a superstar in any process discussion: just make a quick estimate of V and of Y, so you can pinpoint where you are in terms of shear rate and, therefore, viscosity. I like to use a simple adhesive as an example.

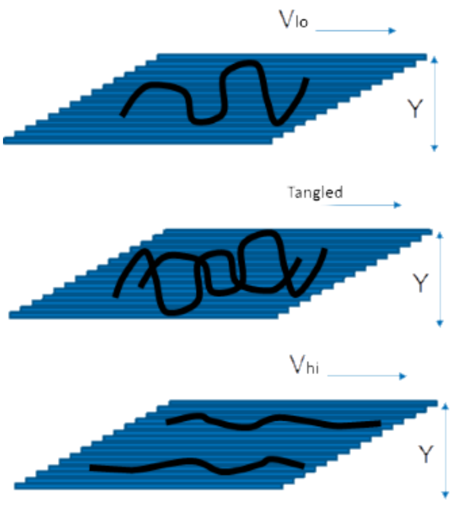
The user opens the cap of the tube and wants to squeeze out the adhesive. You don't want the viscosity to be too low, otherwise it will flood out. Equally, it cannot be too high, otherwise it will be too hard to squeeze. You have your Cross model, now all you need is your shear rate. The tube radius is 0.25cm and you want the adhesive to come out at 2.5cm/s, so V/Y = 2.5/0.25 = 10/s. Now the user needs to get a thin, even layer of adhesive by sliding together two surfaces. We need a really low viscosity for the adhesive to flow nicely. So what is the shear rate? We can estimate 0.5m/s for the act of sliding, and we need 50µm of adhesive, so V/Y=0.5/0.00005 = 10,000/s. For manufacturing who need to mix the adhesive with a stirrer there is no easy way to estimate shear rate; it is well-known that a "high speed stirrer" is somewhere in the range of 100-1000/s.

This sort of quick analysis on your own formulation is very powerful. It combines your knowledge of how the formulation *should* behave with how it *will* behave (as judged by the Cross model and your estimates of shear rate). If your rough estimates tell you that each process is comfortably in the right domain, then no further work is required. If they tell you that one part of the process is problematic, then you have more work to do. If your estimate of shear rate tells you that things are borderline then you need to refine your estimate with some more experiments. For example, if others say that the flow rate from the tube will be 1, not 5 cm/s and your estimate tells you that between 2 and 10 /s viscosity will plummet, then you need to do some serious testing of glue squeeze rates and, perhaps, a re-design of the nozzle. If you know that the viscosity hardly changes across this velocity range then you don't have to do the experiments.

2.1.2 What causes shear thinning?

What is far more interesting than the details of the model is the reason for shear thinning itself. This is important to grasp as it will fit in with much else that rheology has to offer us. The reason for shear *thickening* (walking on cornstarch) is very different and is discussed in the particles chapter.

We start with a discussion of shear thinning in *polymeric* systems which is important in its own right and leads us onto a key theme that deserves our attention because we should be spending more of our rheological time trying to understand it. The shear thinning of *particle* systems does not happen below a specific volume fraction, showing that the flow behaviour of particles is more complex. Particle systems (which may be solids, emulsions or foams) have a chapter to themselves once we have discussed the broad range of rheological behaviours.



We have our streamlines. At low shear values, a polymer in the liquid spans a number of streamlines. Those in the fast stream are being held back by those in the slow stream, so there is a general increase in resistance to flow, i.e. a high viscosity. If the polymers are at a sufficient concentration to tangle then the effect on the viscosity is much higher. At high shear, however, the polymer chains are stretched along the streamlines and are untangled, so resistance to flow is low and therefore the viscosity is low. The reason we need a Cross model with four parameters is that the whole process is complex. The ability for a polymer to tangle depends on its concentration (of course), on its MWt[3] (bigger MWt will tangle more, of course). It also depends on how "entangleable" the polymer is which is more puzzling. For some polymers, a low MWt is enough to tangle, for others it needs a large MWt. If we know the "critical entanglement MWt" then we can predict the low shear viscosity.

Entanglement is important across large areas of formulation space. It is what gives us strong adhesion, it gives us strength and toughness, and it is what (often) stops us from adding as much polymer as we might like because the formulation gets too viscous to handle. For many formulated products and systems, entanglement is good, yet it is entanglement which makes it hard for us to formulate them.

Given that polymers have a critical entanglement MWt, M_c, we should all know their values so we can work out whether we want to be below or above it. The problem is that although values are known for a handful of simple polymers, they are unknown for most of the real-world polymers we tend to use. Until suppliers get into the habit of providing M_c values, we should get into the habit of estimating them ourselves. Two apps help you to do this.

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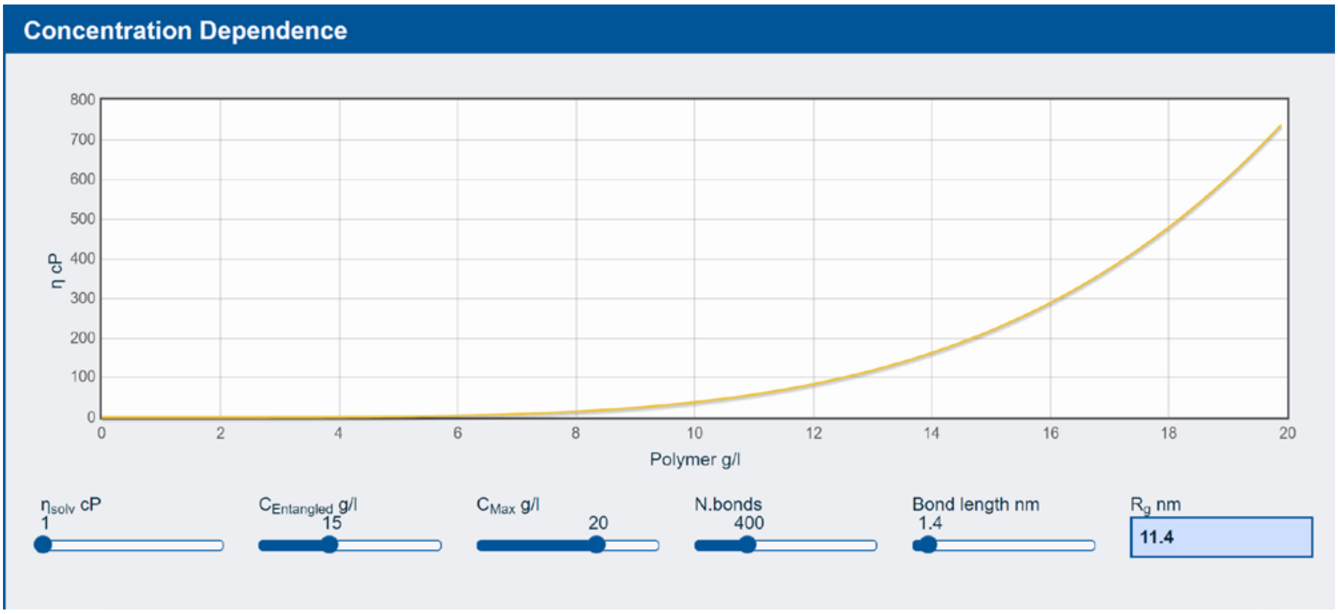
[3] It gets tedious to keep typing molecular weight, so I use MWt.



η_{solv} cP 1
$C_{Entangled}$ g/l 15
C_{Max} g/l 20
N.bonds 400
Bond length nm 1.4
R_g nm 11.4

App 2-2 https://www.stevenabbott.co.uk/practical-rheology/Low-Shear-Polymers.php

The first app uses an approximate formula for how quickly viscosity increases around M_c. There are two fudge factors, A and B, then there is the viscosity of the solvent, η_0 and a radius of gyration described below which depends on a number of pseudo-bonds and pseudo-bond-length (a Kuhn length rather than a molecular length), and, for simplicity, an entanglement concentration, C_E.

Equ. 2-4
$$\eta = \eta_0 A\left(BCR_g^{\ 3}\right)^{1.3}\left(\frac{C}{C_E}\right)^3$$

In the example above, the viscosity is 220 cP at the C_E of 15g/l polymer and doubles to 440 cP by 17.7 g/l, showing how a small absolute change in concentration can have a big impact on the viscosity. As with all these sorts of rheology plots, the viscosity of the base solvent has an unexpectedly large impact. If you increase it from 1 to 2 cP (try it in the app!), the viscosity at 15 g/l does not change from 220 to 221 cP but to 440 cP.

This is an important point. Pay almost as much attention to the viscosity of the base fluid as to the M_c effects - you might be able to avert a viscosity crisis via a change to a solvent rather than to the polymer in the formulation. But beware, the solvent changes the "radius of gyration" of the polymer, R_g. A good solvent allows the polymer to open up (larger R_g), which means that the chains are more likely to tangle. A bad solvent causes the polymer to collapse and tangle less, though you can go only so far with this trick because soon the polymer crashes out of solution.

That breathless paragraph introduces a complex bunch of ideas even though this is the simple version. The next app (from Practical Solubility) shows the full complexity.

R_g @0.5+40K nm 11.53

M_{mono} 100

Polymer MWt 60816

Polymer M_c 7655

Flory-Huggin χ 0.18

C_{max} g/l 20

R_g @χ+MWt nm 20.2

Ne 25.5

C* g/dl 1.2

Ce g/dl 1.6

|η| dl/g 4.09

N.bonds 400

M_{bond} 100

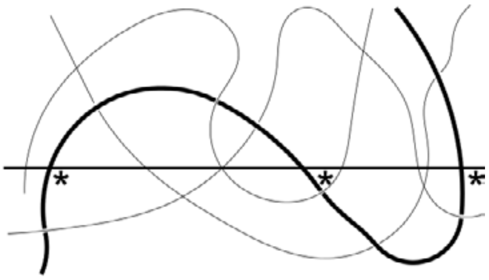
Bond length nm 1.4

MWt 40000

R_g nm 11.4

App 2-3 https://www.stevenabbott.co.uk/practical-solubility/polymer-viscosity.php

This app takes in M_c as a parameter and includes a measure of solvent-polymer compatibility, the χ parameter which goes from 0 (totally compatible, polymer fully expanded) to 0.5 (the polymer is bordering on unhappy). You can read the detailed text of the app to learn more. The point is that although polymer viscosity behaviour is more complicated than we would like it to be, it *is* possible to make sense of it if you put aside an hour or so to understand the key points about χ parameters, radius of gyration, M_c and those Kuhn lengths used instead of real polymer bond lengths.



I have used the term "entanglement" without definition because the intuitive meaning is correct. Formally, a polymer is entangled if at the average arbitrary interface a typical chain crosses it three times, shown by the * symbols in the diagram. With only two crossings you can pull out a chain without creating a tangle. The ability to create a tangle depends on the MWt and on how much the chain tends to fold back on itself and this varies from polymer to polymer. M_c for polyethylene and polypropylene is rather low, just a few 1000, which means they are highly tangled. The same applies to polycarbonate, which is why it is so tough. PMMA and polystyrene both have high (40K+) M_c values so they are not very tangled in the bulk and are easy to crack.

As we will see later on, other rheological (and real-world) behaviours of polymers depend on entanglement so sooner or later it is worth getting to know about it.

2.1 Thixotropy

For classic pseudoplastic shear rate thinning described above, if you pause at any shear rate and keep measuring the viscosity, it remains constant. For a thixotropic material we have two effects - the viscosity decreases as the shear rate increases, and the viscosity decreases if you keep shearing at a given shear rate.

There is an annoying tendency of people to say "thixotropic" when they merely mean "shear thinning". All thixotropic formulations are shear thinning but not all shear thinning formulations are thixotropic.

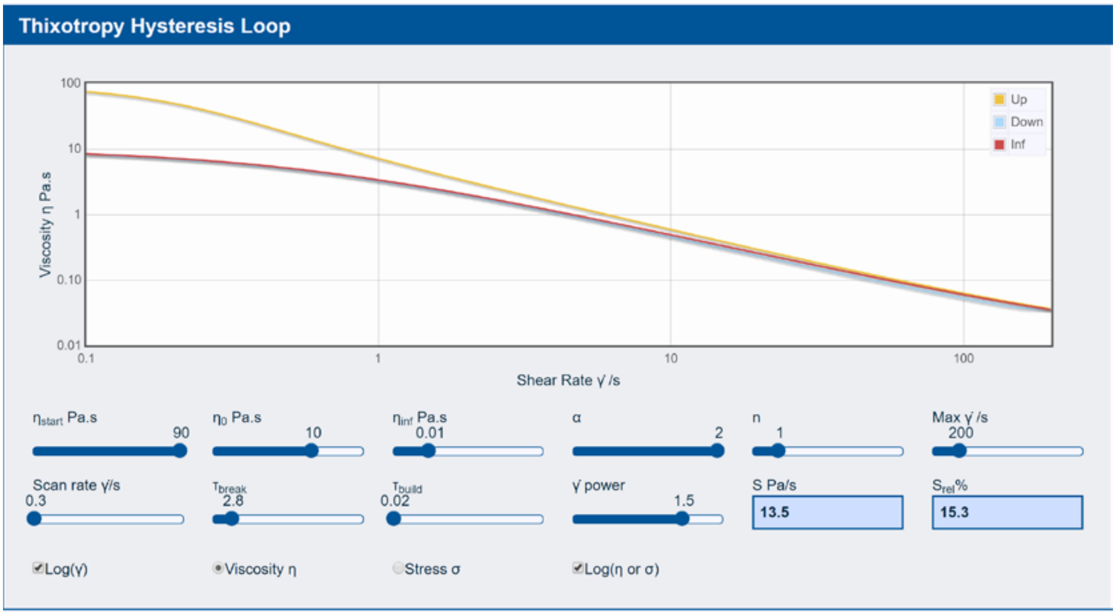
Thixotropy can be a useful feature in a formulation as in classic gel-type paints that are conveniently thick in the pot and on the brush, while flowing nicely with the hight shear of the brush stroke. In some types of printing (especially, it is said, screen printing) it can be useful if it stops the printed features from spreading. My own view on this is that thixotropy is *not* relevant because the timescale for recovery is usually much larger than the timescale for spreading.

Usually thixotropy is a nuisance because we never know, at any moment, what the viscosity really is; different portions of our formulation might have had different amounts of shear for different amounts of time.

It is also a nuisance because measuring it is contentious. At a high-enough shear rate there is no thixotropy because whatever causes it has been sheared into irrelevance. At a low-enough shear rate we are near the contentious yield stress zone, and thixotropy confuses an already confusing system.

If you want to give an objective value to a formulation's thixotropy, to be able to compare samples and to swap data between labs, then, as is so often the case, rheologists have devised multiple methods for measuring thixotropy. You can, for example, do a steady low shear, switch to a high shear then re-measure at low shear to get the decrease in viscosity and a time to return to the original. Or you can do an oscillatory measurement and watch as G' and G" change with rate of oscillation.

This seems to create more confusion than enlightenment, especially as I seldom (or maybe never) see sentences such as "You know what, we looked at a ton of methods then chose this one because ...". People just seem to pluck a method from the air. Well, you know what, I looked at two methods and the first of them appealed to me because it gives a readily measurable numerical value (you can choose between the "thixotropic area" and the probably more precise "relative area") and also gives timescales for structure making and breaking. Because I believe that timescales are under-rated in our thinking about rheology (they feature strongly in the Semi-solids chapter Interconversions chapters) I want to encourage this sort of thinking.



η_{start} Pa.s 90

η_0 Pa.s 10

η_{inf} Pa.s 0.01

α 2

n 1

Max $\dot{\gamma}$ /s 200

Scan rate $\dot{\gamma}$/s 0.3

τ_{break} 2.8

τ_{build} 0.02

$\dot{\gamma}$ power 1.5

S Pa/s 13.5

S_{rel}% 15.3

☑Log($\dot{\gamma}$) ●Viscosity η ○Stress σ ☑Log(η or σ)

App 2-4 https://www.stevenabbott.co.uk/practical-rheology/Thixotropy.php

We start at a low shear rate and measure the viscosity at increasing shear rates during the "up" curve. We then re-measure at decreasing shear rate for the "down" curve. If this is immediately followed by another up and down we might find (as in the example shown) that the down curve has not shifted, so it represent the infinite curve, i.e. what we would find if the system was pre-sheared for infinite time at each shear rate.

We can then fit those curves to a Cross model (that's the infinite curve, defined by η_0 and η_{inf}, α and n as before) plus a value of η_{start} at our lowest shear rate and two relaxation times, t_{break} and t_{build} and a power dependence of t_{break} on shear rate.

This all comes from a simple (that's the authors' word) model[4] for thixotropy. There is only a single formula:

Equ. 2-5 $$\frac{\delta\eta}{\delta t} = \frac{(\eta - \eta_e)^2}{\tau}$$

This tells us that the change of viscosity with time depends on how far you are from the equilibrium or infinite value and on a timescale τ which is assumed to be a constant if it is τ_{build} on the down curve where the structure may be re-building and a structuring timescale τ_s which depends on a constant τ_{break} and the shear rate to a power, p:

Equ. 2-6 $$\tau_s = \frac{\tau_{break}}{\dot{\gamma}^p}$$

With the three values τ_{build}, τ_{break} and power p we have some feeling for what is going on internally. We also have the "thixotropic area" under the curve which is

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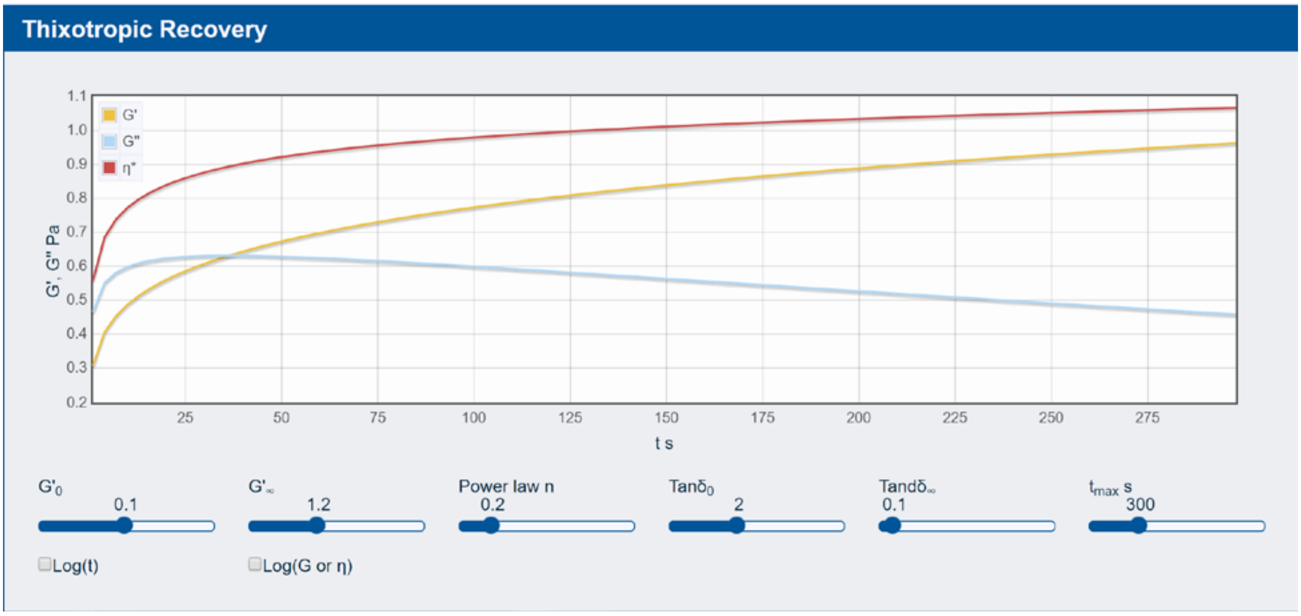
[4] Elaine Armelin et al, *A simple model to describe the thixotropic behavior of paints*, Progress in Organic Coatings 57 (2006) 229–235

some sort of measure, though it is arguably better as the "relative area" obtained by dividing by the area under the up curve.

Out of personal interest, I wrote an app that describes an oscillatory method, giving the G' value with time after stopping a fast shear.

Equ. 2-7 $$G'_t = G'_0 + A.t^n$$

I do not see how it can be of much use because it just gives a power law, n, for the timescale and a value, A which sort of describes the difference in G' after shear and at infinite time. What can I do with such values?



G'_0 0.1

G'_∞ 1.2

Power law n 0.2

$Tan\delta_0$ 2

$Tan\delta_\infty$ 0.1

t_{max} s 300

☐Log(t)

☐Log(G or η)

App 2-5 https://www.stevenabbott.co.uk/practical-rheology/thixotropic-recovery.php

2.1.1 What to do with the relaxation times

A phenomenon such as entanglement imposes a relaxation time. It takes time for chains to slide out of tangles, or to reform into tangles so processes will be much slower. And those who have tried to disentangle a ball of string will know that a sudden, impatient, tug on the string makes matters worse. The tug is faster than the timescale for the chains to slip past each other, so it causes the tangle to tighten. Entanglement, therefore, automatically implies different relaxation times in response to different stimuli. Putting things in reverse, by looking at relaxation times in response to different stimuli, you get a good idea of how that system is behaving internally, for example whether it is tangled or not.

Such understanding can have a significant impact on how you formulate. I will choose a specific example. Your task is to apply the same type of thinking to your own formulation issues.

For much of my formulation life, the main way to thicken something was with a polymer. For reasons unknown to me, the functional behaviours of different polymers differed significantly and I had to resort to trial and error. For example, the effect of MWt of one polymer was very different from that of another.

With hindsight I can see that my ignorance of entanglement was behind my puzzlement. I had never heard of critical entanglement MWt and how it varies wildly between different types of polymers, so I had no intellectual framework to work through the issue of choosing the right polymer. A specific example of this was in screen printing, I was disappointed that recovery of viscosity after shear was so slow. A particle-based ink printed side-by-side with a polymer-based ink behaved much better because the particle-based ink recovered its viscosity near instantly.

I then "discovered" associative thickeners. These were a revelation because their recovery is so much faster. The difference is entanglement. For normal polymers, the tangles that give them their viscosity also slow down their return to viscosity as the chains' ability to move back to their tangled state is increasingly limited by the tangles (this is reptation physics). Associative thickeners are tangled via a network of weak local bonds (such as hydrogen bonds) that can re-form with very little main chain motion. Particle systems recover quickly because there is little need for rearrangement or motion to return to the low-shear state.

All this is obvious with the right language of timescales and entanglement and rather obscure without it.

The implications for the formulator are clear. If you need an entangled system for other purposes (such as adhesion), don't expect fast relaxation times and low thixotropy. Because the amount of entanglement is concentration-dependent, expect thixotropy to change dramatically over a relatively small range around a critical concentration.

If you require viscosity coupled with low thixotropy, then associative or particle thickeners are effective. There is a subtlety with those particle thickeners that rely on strong self-association, i.e. flocculation. An app allows us to explore this subtlety:

$\rho_{particle}$ g/cc 2.5

ρ_{liquid} g/cc 1

$r_{particle}$ nm 208

Wt % 33.7

d_{Close} nm 279.2

d_{Riman} nm 264.1

App 2-6 https://www.stevenabbott.co.uk/practical-coatings/distances.php

The app shows the average distance, d, between particles as a function of wt% of particles. The rate of flocculation recovery depends on the probability of particles touching. If you have a given volume of particles as large radius spheres, d is, on average, large, so it will take a long time for them to travel the distances needed to flocculate, and recovery will be slow. Particles with the same volume and a small radius (move the slider to see the effect of $r_{particle}$) are closer together so need to travel less far.

The app is based on wt%, a more real-world measure. If the density of the particle increases, d *in*creases, because there is less volume fraction. The distance is proportional to radius, so halving the radius halves the distance and at least halves the recovery time (smaller particles also diffuse faster). One subtlety is that the distance reduction effect gets smaller as you increase the wt%, so the gain in recovery time due to interparticle distance becomes less.

One of the joys of writing is the discovery of things I should have known but didn't. I had never previously coupled the Distance app with anything to do with rheology. As I tried to explain to the reader why this sort of logical analysis was helpful, it led me to think through my own logic and recall that I had written the Distance app many years ago. Although the conclusions are rather obvious, having the app made it much easier for me (and I hope for you) to think through the chain of logic.

2.1.2 What to do with thixotropy measurements

Now you know how to analyse thixotropy and have some idea of the root causes and timescales, the question is, what do you do with the knowledge?

The answer is that you think through each stage of your process and decide whether thixotropy is a positive advantage (as it sometimes is for, say, gel paints), or irrelevant (if you are lucky) or a nuisance (which it often is).

The formulator's life is always one of trade-offs. As mentioned above, polymer entanglement is often wonderful for the properties of the end product and a nuisance both in terms of absolute viscosity and thixotropy. Without a knowledge of the causes and effects, formulators (and I have done this myself) try a little bit of this and a little bit of that in the hope that the problems will go away. Sometimes this works, though it leaves a problem for future formulators who have no idea which "little bits" within the formulation are vital, and which are there to cover the problems of other little bits.

By formulating with a knowledge of cause and effects, with some clear thixotropy relaxation time data recorded in your lab notes, along with some plausible formulation hypotheses based on entanglement and relaxation time, the chances are higher that you, and those who follow you, will end up with happier formulations.

3 Yield Stress

What problems are we trying to solve?

Some of us need formulations that flow under all circumstances. Others need formulations that, untouched, just sit there unmoving, but start to flow under some gentle pressure. Those liquids that just sit there till pushed are said to have a Yield Stress, σ_y and we need to be able either ensure there is no yield stress or to control its value so that it is just right for the application.

In fact, all materials yield under sufficiently long timescales and all are rigid over short timescales. In this chapter we focus on "normal" timescales and worry about other timescales in the Semi-Solids chapter.

The plots of viscosity versus shear rate can tend towards high viscosities at very low shear rates because $\eta=\sigma/\dot{\gamma}$ which tends to infinity as $\dot{\gamma}$ becomes small. In any case, often the measurements at these low rates are meaningless because the system at rest isn't viscous - it is solid.

We therefore have the apparently simple idea that some liquids are solids at rest and only become liquid when they are forced to yield via some sufficient stress.

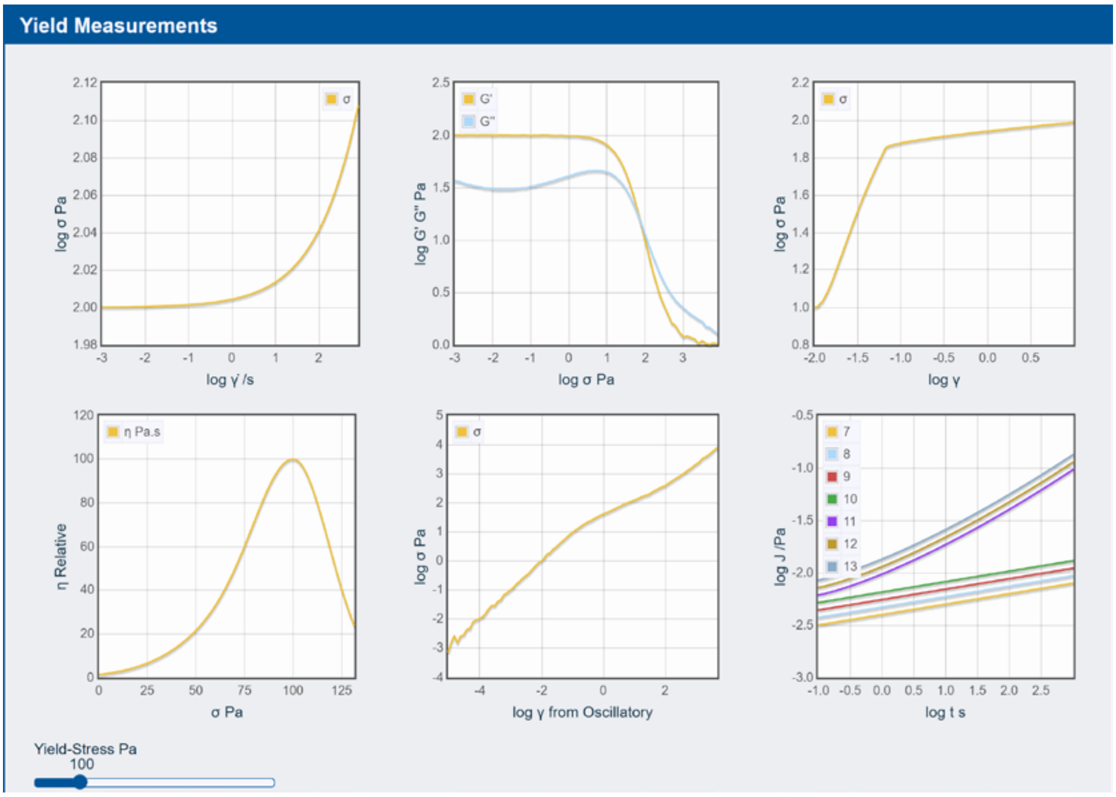
This gives us the useful idea of "the" yield stress of a formulation. This is defined as the stress we have to impose to make the formulation change from an elastic solid to a plastic (flowing) liquid. The classic example is a hand cream. If it has no yield stress it is perceived as being not a "rich" formulation as it just flows in the pot and on the hand (more like a hand lotion). If it has a high yield stress then it is perceived as being not a cream at all because it is difficult to rub into the hands. With the right yield stress it looks solid as a blob on the hand, yet it rubs in smoothly.

The same can be said about foods such as mayonnaise. With no yield stress it is too runny to be acceptable (and falls off your frites or hamburgers), with a high yield stress it cannot be easily poured or spread over the food.

The problem with yield stress is that there is no way to measure it unambiguously. When we say that it doesn't yield below a certain stress, how can we be sure? If it creeps over a day's experiment at low stress, has it yielded or has it merely crept? This question of timescales for measurements is a key issue, with a chapter all to itself.

We should, therefore, just accept that it is no big deal that yield stress measurements are rather subjective and should mostly be thought of as good-enough indicators of whatever phenomenon interests us in the sorts of timescales that interest us. All we then need to do is to check how they are measured. Here we hit a typical problem of rheology. Read a bunch of papers on yield stress and you will find measurements being made in a bewildering variety of ways, each stated with confidence as being "the" way of doing it, with no indication of why that method was chosen over others that might be equally good or bad. The apparent variety is even larger because of the rheologists' delight in plotting the same data in different manner, so it is even harder to work out what is going on.

Fortunately a wonderful paper[5] from Daniel Bonn's group at U Amsterdam describes many of the different ways, making it easy for me to write an app that shows what you would see if you measured the same yield stress, σ_y, (as an input to the app) in six different ways. Whenever I have to read a yield stress paper I go back to my app to find the nearest approximation so I can make sense of the paper and, perhaps, compare it with measurements on similar systems which have used a different method.



App 3-1 https://www.stevenabbott.co.uk/practical-rheology/Yield-Measurement.php

The first method (top left) is a sort of direct method because it uses the Herschel-Bulkley equation, mentioned in the previous chapter, which contains σ_y as a parameter which comes from fitting the plot of stress versus shear rate. Here is the equation again:

Equ. 3-1 $$\sigma = \sigma_y + K\dot{\gamma}^n$$

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[5] Maureen Dinkgreve, José Paredes, Morton M. Denn, Daniel Bonn, *On different ways of measuring "the"yield stress,* Journal of Non-Newtonian Fluid Mechanics 238 (2016) 233–241.

In a real experiment, K and n are fitting parameters. In the app they are set to plausible values of 1 and 0.5. Other curves, such as Casson, can be used - they are each approximations, with different industries deciding that one type is better than another. The world of chocolate, for example, use the Casson method, even though there is a detailed paper from the industry explaining that Casson doesn't really work well for chocolate. The n=0.5 I have chosen for Herschel-Bulkley is the same dependence on shear rate as Casson (which also uses the square root of σ_y).

The second method (bottom left) takes the same experiment but somehow extracts a viscosity from the data and plots that against σ. I confess to not knowing how this is done, so the values in the app are plausible (I checked with some papers) without being calculated. Maybe it is so obvious how to extract η that the authors did not have to explain. I will happily update the app and this paragraph if someone would enlighten me.

The next technique provides three ways of extracting a value from the data. The basic experiment to measure G' and G'' will be described in the Semi-Solids chapter but hopefully readers are at least aware that these are standard values obtained from oscillatory rheology. The stress is steadily increased (so the best machine is a controlled stress machine rather than controlled strain) until there is an obvious change in the measured parameters. Now we can extract the values by whichever technique we happen to prefer. The first two methods use the data from the top-middle, the third uses data from the lower-middle plot:

1. Very popular, because it is simple for humans and computers to spot it, is to take σ at the cross-over point when G'' becomes larger than G', i.e. the system becomes more viscous than elastic. This value is usually an overestimate and is sometimes called the Flow stress rather than yield stress.
2. More true to σ_y is to identify when the G' value starts to decrease which, by definition, means that it's starting to lose its elastic nature. This is tricky to do by computer and rather obvious by the human eye.
3. Because rheologists love to plot data in other manners, the complex strain, γ*, is calculated as Stress/Modulus, i.e. σ/G* where G* is the complex modulus given by $G^{*2}=G'^2+G''^2$. It is said that you can see σ_y from intersection of the two relatively straight lines.

Next (top right), you set up a (very) small shear rate and watch how stress grows with strain. The yield stress is the plateau value where the strain just keeps going.

Finally (bottom right), you can do a set of creep experiments where you set a fixed stress σ and measure how strain γ evolves. You plot compliance, J = γ/σ versus time, and for a purely elastic material this is a constant, though for real-world materials there is a slight slope with increasing time. At the yield stress, the material can flow so J increases more significantly over time. You can therefore work out from a set of plots a value for σ_y. If you guess badly about the range of σ values to test you might miss σ_y. With a smart setup you would do a low and high scan then do a binary search to get to a precise answer. It sounds a lot of work, but some people like the technique.

Which is the best technique? There isn't one. It depends on the capabilities of your specific system, on the behaviour of the material you are testing and on whether your industry has a standard test methodology. My conclusion is that if your current method is good enough and convenient (or forced on you by industry standards), carry on using it. If you have time to play and find that an alternative method is easier, then do a rough correlation of values between the two methods then swap to the newer method, using the correlation to help compare to historic values.

Above all, keep clear *why* you need these values. If the process of interest to you has no dependence on yield, then don't even bother to do the measurements. Similarly, if the stresses and strains in the measurement technique bear no relationship to those of the system of interest, maybe it is time to choose a different technique.

3.1 Yield Strain

If you strain anything enough it will yield, so if you wish you can measure the yield strain of a sample.


Yield Strain

G'0 300

Yield Strain % 5

Tanδ0 0.3

Yield Stress Pa 15.7

☐Log(G)

App 3-2 https://www.stevenabbott.co.uk/practical-rheology/yield-strain.php

One method is to set up a conventional G':G" oscillatory measurement with steadily increasing stress and spot where G' starts to fall - that is the yield strain. You automatically get the yield stress from γ.G*.

Whether you measure yield stress or strain depends on what question you are trying to answer.

3.2 Using yield stress or strain values

For many formulators, yield stress is a non-issue and this chapter can largely be ignored. For some, it is a vital parameter for a product such as the hand creams or foodstuffs discussed at the start.

The science of predicting/controlling yield stress is difficult, and I have, sadly, had little to say about it, though when we come to particulate systems the situation is better. My concern here is with two issues.

1. Ensuring that your measurement really relates to the end product performance. This often involves consumer test panels who poke, rub, lick or otherwise interact with a range of different formulations and say which they prefer. With luck you can relate that to an objective measure of yield stress.
2. Ensuring that your objective measure of yield stress is comparable between labs, between operators and between samples - in other words that it has a reasonable Gauge R&R[6], showing that the noise in the measurement is less than the signal. Trying to hit a target of 43 Pa when measurements vary randomly between 30 and 60 is not a great way to formulate.

The fact that we have at least six methods of measuring yield stress is a clue that measurement is difficult. The only encouragement I can offer is that *you are not alone*. I have not met anyone in the yield stress world who is happy with those two issues. A famous paper on chocolate yield stress[7] involving a world-wide team and some high-powered labs found many ways in which yield stress is frustratingly hard to measure (the paper does not cover the impact of yield stress on consumers).

One final tip I learned from the experts. If you spend a large amount of time worrying about the precise details of Herschel-Bulkley or Casson etc. the result will be that it really makes no difference compared to getting a good-enough, robust method that works day-to-day on real-world samples. Combine that observation with the fact that you are not alone in your frustrations with yield stress and, with luck, you'll be able to say that good enough is good enough, and get on with your formulating.

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[6] Gauge Repeatability and Reproducibility - found in any reputable process control statistics package. It is amazing, and depressing, how many "industry standard" tests fail elementary Gauge R&R analyses and are, therefore, unfit for purpose.

[7] J.-M. Aeschlimann and S.T. Beckett, International Inter-Laboratory Trials to Determine the Factors Affecting the Measurement of Chocolate Viscosity, J. Textural Studies, 31, 541-576, 2000

4 Semi-Solids

What problems are we trying to solve?

Many of our formulations are neither pure solids nor pure liquids. So we need to be able to understand how much they are of one or the other. A straightforward measurement of G' and G" will do this for you. But it is missing a key point. *Everything* is a solid at a low-enough temperature or a short-enough timescale and *everything* is a liquid at a high-enough temperature or a long-enough timescale.

Because most formulations have to perform under different timescales (e.g. a pressure sensitive adhesive must stick quickly yet not creep over long times), we need to be able to both measure *how* things change over temperature and time, and understand *why* they change so we can formulate intelligently.

There are no such things as solids. At a high-enough temperature (obvious) or a long-enough timescale (less obvious) "everything flows", *παντα ρει, panta rhei* from which we obtain rheology.[8] The prophetess Deborah in Judges 5:5 stated that "The mountains flowed before the Lord", meaning that in a long-enough timescale everything flows. Not explicitly pointed out by Deborah is that mountains also flow if they get hot enough.

We therefore end up with the Deborah number $De = t_{relax}/t_{observed}$, i.e. the ratio of the time over which the system relaxes to the time over which the system is observed. When De is large, the object is a solid, when it is small, the object is a liquid. Water observed on a picosecond timescale is a formidable solid[9] and a mountain on a billion year timescale is a liquid. Reduce the temperature and water becomes a solid with a glacial relaxation time, and at high temperatures a mountain becomes lava which can be a liquid even at a ms timescale, though chemistry and temperature may require measurements on timescales of seconds, minutes or hours[10].

If, at normal temperatures and timescales we have a liquid, our default is to measure its viscosity. If we have a solid, our default is to do tensile testing for its modulus. If you are reading this guide then you probably have a semi-solid

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[8] The delightful note on παντα ρει and the origins of the Deborah number can be found in Markus Reiner's account in *The Deborah Number*, Physics Today, 17, 62 (1964). There is a problem faced back then which has re-surfaced in a different form for the 21st century. Reiner used to get letters addressed to the Theology Department. The sure sign that a rheology pdf has been created by OCR is when you find the word "theology" within it.

[9] There are many stories about the lab in Wales that measured the high-speed properties of water, using a gun to fire bullets into the water.

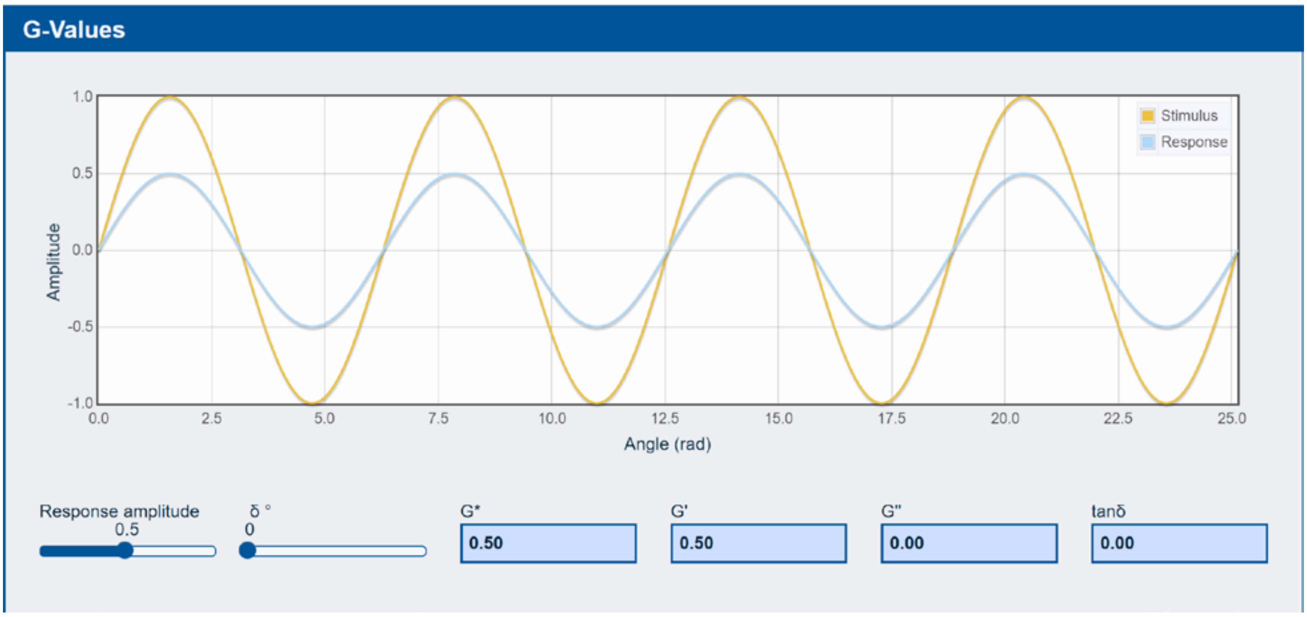
[10] Those lavas that seem not to be moving but over a couple of days can spread over a small village.

with a mixture of properties that will vary strongly with temperature and with timescale.

The classic way to get at this mixture of properties is via G' and G''. As these are easily described,we can spend most of this chapter discussing why other ways of looking at the properties of semi-solids should be a normal part of our rheology repertoire and of ways of thinking about materials in general.

4.1 G', G'' and tanδ

The mixture of fear and ignorance about G' and G'' is unnecessary and unfortunate. They are simple to understand and are powerful indicators of key aspects of many formulations. Most of us are happy with E, the tensile modulus, which is simply stress/strain, where the strain is *along* the material sample. G is the shear modulus, stress/strain, with the strain being *across* the material. So there is nothing mysterious about G values in general. The reason we have G' and G'' is that we need to describe the stress response to the strain (or strain response to the stress, which gives us equivalent terms J' and J'' discussed later) in terms of a purely elastic term, i.e. as if it were a pure solid, and a purely plastic (or viscous) term as if it were a pure liquid. We can best describe how this comes about with an app:



Response amplitude 0.5
δ ° 0
G* 0.50
G' 0.50
G'' 0.00
tanδ 0.00

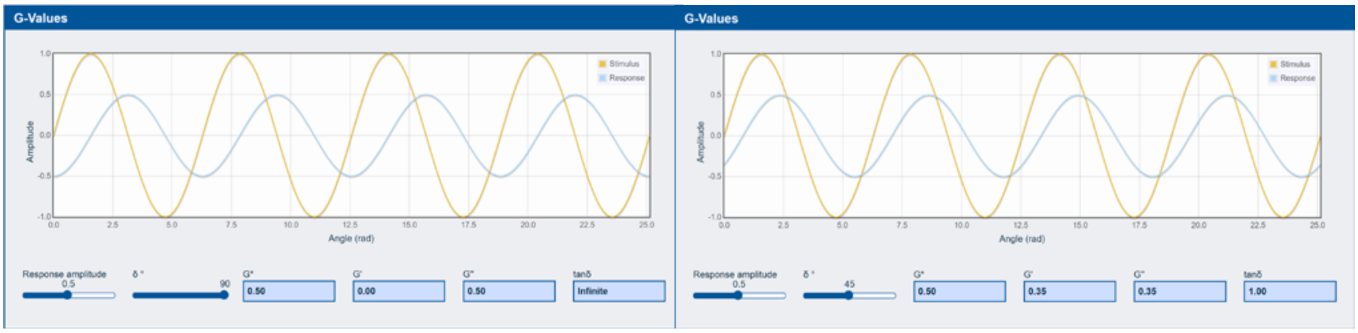
App 4-1 https://www.stevenabbott.co.uk/practical-rheology/G-Values.php

We have the sample squeezed between two plates, one of which can oscillate. We might oscillate it with a known maximum stress or maximum strain, creating a stimulus. We measure the response either as a stress on the lower plate (for oscillating strain) or as a rotational speed (strain rate) on the plate to which a known stress is applied. These are, respectively, the controlled strain and controlled stress rheometers, with endless discussions about which is better or better value for money.

For the measurement of G' and G'' the official tradition has been to oscillate the strain and measure the stress; doing it the other way round, oscillating the stress, is equivalent to measuring J' and J'' discussed briefly below. Because precise conversion between G and J is possible, we can feel free to choose whichever type of machine best suits all the other things we need from our rheometer. In any case we either have whatever rheometer we have, or modern technology is making the differences in price and performance between controlled stress and controlled strain machines ever smaller.

In the image above, the stimulus creates a response of amplitude 0.5 (again, we don't care about the number or units at this stage). The important point is that the response exactly follows the stimulus - it is "in phase", with a phase angle, δ = 0. This is what a pure elastic solid does. The total G value, shown as G* is 0.5 (i.e. our response amplitude) and it is made up of a G' of 0.5 and a G'' of 0. So G' is our purely elastic response.

Now let us look at the images of two other possibilities:



Response amplitude 0.5
δ ° 90
G* 0.50
G' 0.00
G'' 0.50
tanδ Infinite

Response amplitude 0.5
δ ° 45
G* 0.50
G' 0.35
G'' 0.35
tanδ 1.00

Figure 4-1 On the left we have the response 90° out of phase - this is a pure viscous response. On the right the phase is 45° and we have equal elastic and viscous components.

With a pure liquid (left plot), the response is exactly 90° out of phase, so δ = 90. Here's the reason. As we know, the stress in a viscous fluid is proportional to the velocity. When the stimulus is at a maximum it is changing from one direction to another and its velocity is 0, therefore the response (viscous stress) is zero. When the stimulus is at zero it is at maximum speed heading towards the minimum, so maximum speed means maximum viscous stress. Therefore the response is 90° out of phase. G* is still 0.5 and now G' is zero (no elastic component) and G'' is 0.5.

In real materials we tend to have a mix of both. That is what we see in the image on the right. The response is now 45° out of phase. This means that we have equal elastic and viscous responses so G' = G'' = 0.35. The reason that the responses are not 0.25 is that G* is defined by $G^{*2} = G'^2 + G''^2$. The reason for this is that G* is a complex number (the "complex modulus"), with G' being the real component and G'' being the imaginary, though we don't need to be distracted by such issues.

The other number shown in the app is tanδ, the tangent of the phase angle which is G''/G'. When δ = 45°, tanδ = 1 and we have equal components from the elastic and viscous elements.

Armed with this straightforward information you can now tell at a glance from a typical oscillatory rheometry plot how the system behaves as parameters (such as temperature) are systematically changed. If tanδ < 1 then the system is dominated by elastic behaviour and when tanδ > 1, the system is dominated by viscous behaviour.

When, for example, the G' line dips below G'', that is an indication of a significant change. We have seen this in one form of yield stress measurements. For classic polymers the temperature at which this happens is the glass transition temperature, Tg. When you find the conditions on the graph that apply to your formulation you will know whether it is mostly elastic or mostly viscous.

4.1.1 Storage and Loss

So far I have described G' as elastic and G'' as viscous. I could also call G'' plastic, which allows us to talk about the "elastic and plastic" components. Plastic in popular language means something that doesn't easily flow (a plastic bag returns to its original shape once the shopping is removed from it), but in technical language it means irreversible flow as in "plastic deformation".

The other common terms are "storage" for elastic and "loss" for viscous. A purely elastic material stores the energy under strain and returns 100% of it on release. A purely lossy, viscous material has no recovery after being strained and all the energy has been lost as heat.

You can feel free to choose whichever pair of terms pleases you; you just need to be aware that others might choose a different pair.

There is, however, a catch. To say that your formulation is "mostly elastic" or "mostly viscous" is true only for a specific set of conditions. Your formulation is likely to pass through a wide range of conditions so you need to know how the relative elastic and viscous proportions will change. For that we need to return to the Deborah number.

4.2 TTE/TTS/WLF

Ignoring practical realities, if we could measure water with our plates oscillating at greater than GHz frequencies, we would find a respectable G' as well as some of the G'' we think of as normal for water. Or with plates oscillating over the billion year timescale, a sample of rock would have a respectable G'' as well as the G' of normal rock. So G' and G'' are not an intrinsic characteristic of a material - they are frequency-dependent or Deborah number dependent, whichever way you prefer to think about it. Similarly, at normal frequencies, water has a respectable G' below 0°C and rock has a nice G" above 1000°C, so we have a temperature dependence as well.

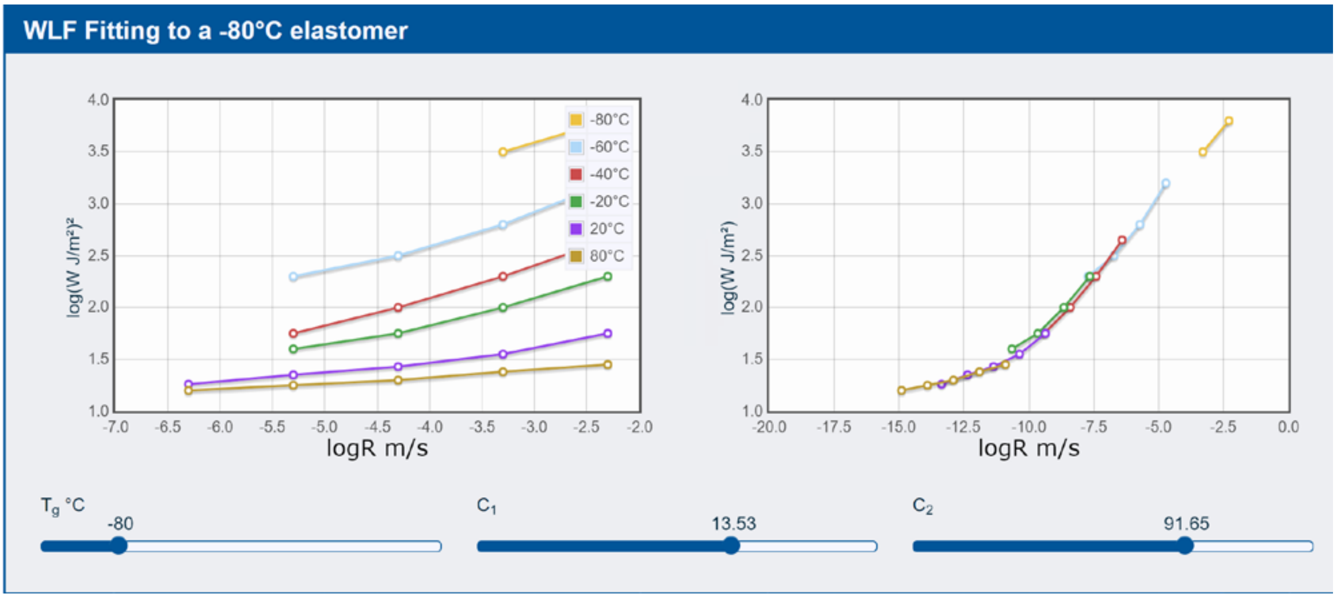
Returning to reality, in a typical rheometer we can measure only a narrow range of frequency and temperature. Let us say that our specific rheometer can only cover 0.01 to 10Hz and -10 to 80°C. Fortunately, we can create measured values over a much larger *virtual* range. For example, a measurement made at 0.01Hz at 80°C might be like a measurement made at 0.0001Hz at room temperature. Think about it; at high temperatures things flow and at low frequencies things flow, so the 80°C measurement is rather like a very slow measurement at room temperature. Going in the other direction, a measurement at -10°C and 10Hz might be like a measurement at 100Hz at room temperature, because things are more rigid at low temperature and at high frequency. So our limited rheometer can now, effectively, measure from 0.0001 to 100Hz.

The fact that time is equivalent to temperature or that you can superimpose time-related data with temperature-related data is well-established across a remarkable range of practical materials and you can generally assume that it applies to your specific formulation. We therefore invoke TTE (Time Temperature Equivalence) or, according to local preferences, TTS (Time Temperature Superposition). If you want to appear super-smart you can call these tTE and tTS because time is usually a small t and temperature is usually a large T. To do the calculations we invoke WLF, the Williams, Landell, Ferry equation:

Equ. 4-1
$$Log\left(a_t\right)=\frac{-C_1\left(T-T_r\right)}{C_2+T-T_r}$$

We have two positive constants, C_1 and C_2 a reference temperature T_r and at our given temperature T we can calculate a_t. The equation is simple, but what does it mean? Let us start with $T=T_r$. $Log(a_t)=0$ so $a_t=1$. This means that whatever our real measurement timescale is (say 1Hz) we multiply the result by 1, i.e. it is not shifted. If $T>T_r$ then $Log(a_t)$ is negative, let us say that it is -2. That tells us that a_t is 0.01, which means that from our 1Hz measurement our effective frequency is 0.01Hz, i.e. this higher temperature measurement is equivalent to a measurement made at our reference temperature at 0.01Hz, which makes sense because higher temperature is equivalent to lower frequency.

So WLF allows us to transpose measurements at different frequencies and temperatures into a single plot equivalent to a wide range of frequencies at a fixed temperature or a wide range of temperatures at a fixed frequency. We can see this with an app.


WLF Fitting to a -80°C elastomer

T_g °C -80

C_1 13.53

C_2 91.65

App 4-2 https://www.stevenabbott.co.uk/practical-rheology/WLF.php

The data on the left aren't rheology data, though they could be - WLF is a universal phenomenon. They happen to be a set of adhesion peel energy curves versus the rate, R, of measurement done from -80 to 80°C. At high temperatures the adhesion is low because the polymer is soft, at low temperatures it is high because the polymer is rigid. Adhesion increases with peel speed. So we have 6 curves which are very nice, but hard to fit into a big picture of what is going on. By knowing that in this case T_r = -80°C and by playing with the C_1 and C_2 sliders it is possible to create a single WLF curve, where the colours of the different portions (which can overlap) relate to the colours in the original graph.

The WLF curve tells us what the peel would be at -80°C at a rate of 10^{-14} m/s. And that is a nice give-away. You often see impressive G':G" plots spanning a vast frequency range and you can imagine that they must have an amazingly good rheometer - until you think about the timescale on the graph. In this example, if the peel measurement was made over 1cm then the experiment would have taken 10^{12}s, i.e. ~30K years. In rheology plots created via WLF the frequency range might start at 10^{-6} Hz. If you needed 10 oscillations to make a measurement, then that one data point would take 10^7 seconds, a third of a year.

What do C_1 and C_2 mean? C_1 tells us by how much a property changes over our temperature/time range of interest. If it equals 7 then that tells us that there is a range of 7 orders of magnitude in, say, modulus, taking it from 1 GPa (10^9 Pa) to100 Pa. C_2 is half the temperature range over which that C_1 range takes place. If C_1 is 7 and C_2 is 40 then over a 40°C range the modulus will have changed by $10^{3.5}$.

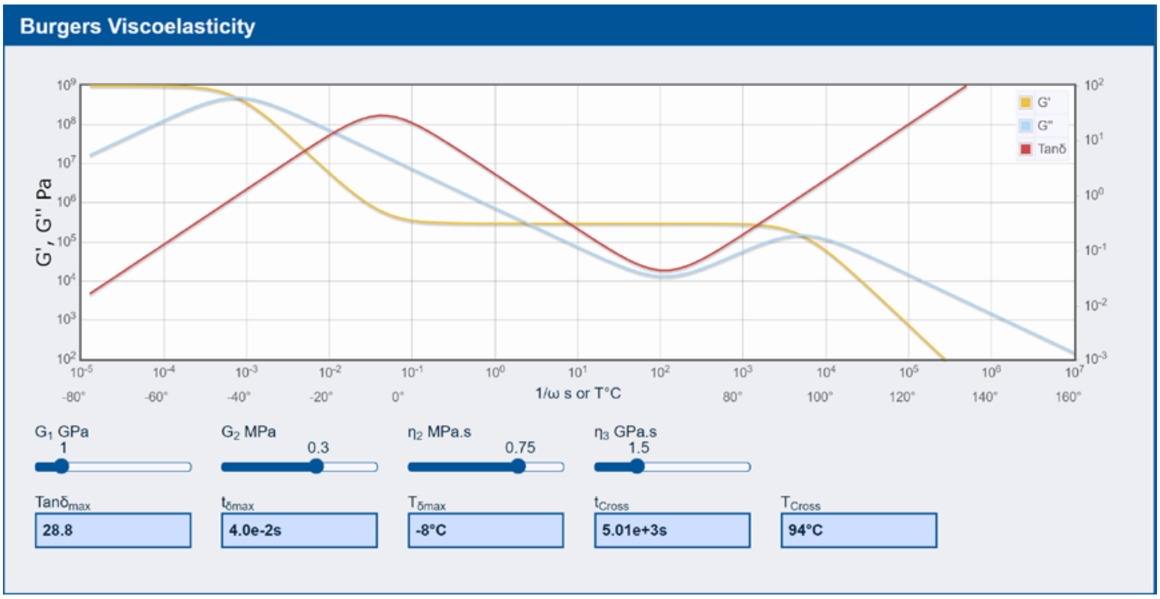
4.3 How do we use G':G" and WLF information?

Does any of this have any contact with reality? I will answer that question with a specific example from my own experience.

I had been talking to a team working on a pressure sensitive adhesive, PSA. I had pointed out in theoretical discussions how the WLF version of the results would help understand the adhesive properties.

I was then asked to stop talking and start demonstrating the effect in their lab. It had been 10 years since I'd last used a rheometer and we could not find the WLF software on the machine. So we gathered some data, realised it was wrong (I had set too low a strain), re-gathered the data, then late at night in my hotel room I wrote an Excel spreadsheet to do the WLF transform. [That spreadsheet, having removed any commercially sensitive information, has proved a very popular download from the WLF page]. The next morning we were able to look at the overall picture of the adhesive across a wide frequency range and things started to make sense. We also found the WLF software on the machine and, happily, the results were the same.

What does the overall picture look like? For this type of adhesive and for many other real-world formulations, it looks rather like the following which is an idealised Burgers viscoelastic model based on ideas (acknowledged in the app) of Roelof Luth:



G_1 GPa 1

G_2 MPa 0.3

η_2 MPa.s 0.75

η_3 GPa.s 1.5

$Tan\delta_{max}$ 28.8

$t_{\delta max}$ 4.0e-2s

$T_{\delta max}$ -8°C

t_{Cross} 5.01e+3s

T_{Cross} 94°C

App 4-3 https://www.stevenabbott.co.uk/practical-rheology/burgers.php

Notice, first the large range of timescales (plotted as 1/ω where ω is the frequency) and the equivalent large range of temperatures - this is clearly an idealised WLF plot. Next, note that the whole G' and G" data can be described by four parameters. G_1 is the low temperature or high frequency plateau ~1GPa. G_2 is the broad middle plateau for G' around 0.3MPa which happens to be ideal for a pressure sensitive adhesive. Then we have η values which affect the two declines in G'. The first of these sets the Tg, the second sets something like the melting point. In the next chapter we shall see that being able to describe a material with just two G:η pairs is unusual - it generally requires multiple pairs spread across a large timescale range.

If we all had full plots such as these for our formulations we would know how they behaved with sudden shocks (high frequency) or over large timescales, or low or high temperatures. These plots are a super-compact way of providing answers to a lot of questions - within the limits of the assumption behind the measurement which is of small strains.

For those who remain cynical about all this and regard WLF plots as some sort of physicist's game unrelated to reality, I have one more thing to say about PSA. You can create Burgers-style G':G" plots via WLF. But what do they have to do with the important issue which is the adhesion of the PSA? The answer is "a lot". You can measure the same PSA's adhesion over a large range of temperatures and times and create a single plot via WLF. When you do so, you find that the three parameters, C_1, C_2 and T_r are identical for the rheology and adhesion datasets. So at a very fundamental level, adhesion, WLF and the Burgers model are inter-related.

4.3.1 Your own G':G", WLF insights

You may recall the idea from an earlier chapter of becoming a superstar by being able to do rough calculations of shear rates and, therefore, knowing what your viscosities might be at different parts of the product's lifecycle. You can (and should!) do a similar analysis for your semi-solid formulations. For example, for PSAs it turns out (and we will discuss it more in the next chapter) that even such an approximate analysis is of great help to the formulators. Here is the logic:

- What are the timescales of PSA processes? The key process of sticking has to be around 1/s, you need it to stick "immediately". Now imagine peeling a piece of adhesive tape for an adhesion tape test at 1 cm/s. The thickness of the adhesive is (in round numbers) 0.01 cm, so we are ripping it apart at 1/0.01 ~ 100 /s. If we apply a weight to the tape so that it is being sheared, we are worried about velocities of 10 cm/day, or around 10^{-4} cm/s, giving us 10_{-4}/0.01 ~ 0.01 /s.

This rough analysis tells us that at the very least we should understand the G':G" behaviour over a 0.01 to 100 /s timescale. A large G" at the 0.01 /s timescale would be as catastrophic (easy shear) as a small G' at the 100 /s timescale (insufficient peel strength). It also turns out (the so-called Dahlquist criterion, https://www.stevenabbott.co.uk/practical-adhesion/dahlquist.php) that a G' greater than 0.3 MPa at 1 /s renders a typical PSA too slow to stick quickly.

As has been shown many times in the PSA world, getting the right G':G" at all three timescales does *not* guarantee success - PSAs are far too complex. On the other hand, having any of those three wrong *does* guarantee failure.

I can therefore say with certainty that if your product has to perform at different timescales (and few products don't), you will gain a large benefit from a quick analysis of what those timescales will be and what general G':G" values are needed. By meeting those general requirements, success is *not* guaranteed; failing to meet them *is* guaranteed to render your formulation sub-optimal.

It is highly likely that to get the values at all relevant timescales will require some WLF work. Trust me; if I can do it with zero notice late at night with no app to help me, you will have no problem doing it if you can create the quality time away from daily pressures of formulation to become comfortable with a WLF analysis of your own system. Your rheometer probably has some presets that will do a good-enough job with almost zero effort on your part - they will have been there from day one, ignored and unloved because no one understood why time temperature superposition would ever be of any relevance to anyone.

4.4 Are G':G" all we need?

So far it would seem that rheology is just about viscosity, yield stress and G':G". The overwhelming number of rheology measurements are taken using these techniques and they do a good job. But we are seriously missing out on a deeper understanding of our formulations if we think that that is all there is.

I have spent most of my life staying away from most other measurements because I could not see the point of doing them except when they were answering a very specific question. For example, if I was interested in whether a material would creep (slowly extend under load) over time, I might consider a creep measurement.

My view of these measurements changed instantly when I was watching one of the excellent TA Instruments webinars[11] where it was pointed out that different techniques were mathematically interconvertible, which meant that data measured conveniently by one method could be converted to a different format (e.g. the G':G" format) that might be more insightful but which would be inconvenient/impossible to obtain on a specific rheometer.

This means that we can start asking bigger questions and use a variety of convenient techniques to get big picture answers. At least in principle. As the next chapter describes, life isn't quite that easy.

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[11] https://www.tainstruments.com/strategies-for-rheological-evaluation-of-adhesives/

5 Interconversions

What problems are we trying to solve?

Semi-solids can do many things such as flow, creep and relax. The first problem is that if you think of each behaviour as something separate (e.g. you do G':G" measurements and, on a different machine, creep measurements) you are missing out on a lot of information. The more important problem is that each type of measurement has a natural, convenient timescale so it might not be possible to get, with one technique, the data you want concerning a timescale that is important in your formulations.

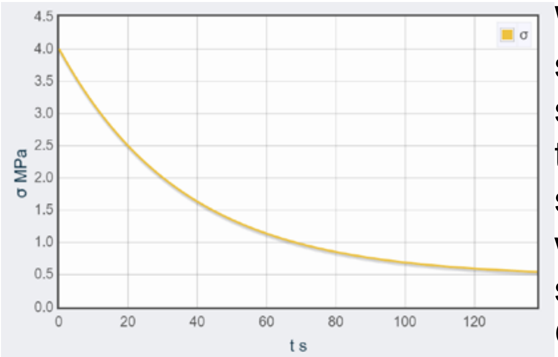
It turns out that all these behaviours are mathematically equivalent so, in principle, a measurement of, say, creep over one timescale, can tell you about G':G" behaviour in cases where that timescale is not readily accessible. It also turns out that we can get a grand view of these processes via "spectra" with respect to time. We therefore have the potential to combine and interconvert our separate measurements into whichever views provide us with the fullest insights into our formulation challenges.

Everyone, except me, knew that it was possible to convert between rheological measurements. Once I had found this out for myself I read many papers saying why interconversion method A is no good and how method B is better, without actually telling me how to do it. This is a reflection of the academic ethos which accepts that it is OK to publish a complicated paper on a topic that is said to be of real-world importance (which justifies doing the research) without having to include any consideration of whether anyone will ever use that research. All of us who formulate could really benefit from being able to grasp interconversions and use them to our advantage. Yet the academic community seems not to have cared, other than (and I applaud this) providing some algorithms to the few companies large enough to sell rheometers and the associated software.

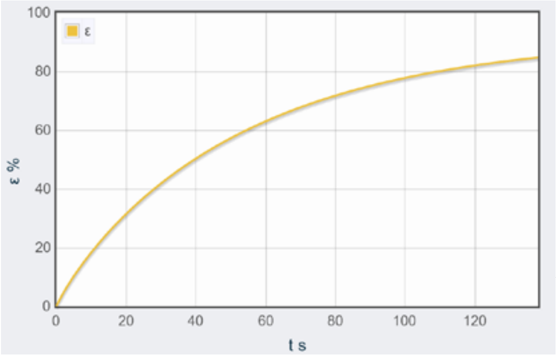
I do not have the brain power or mathematical training to do the job that the specialist academics should have done. But at least I have made an interconversion app that shows the possibilities and discusses the principles. My own grasp of the key inter-related concepts in rheology has improved greatly during the creation of the app and my aim in this chapter is to persuade you why you should be interested in the ideas and, ideally, influence the rheology community to make interconversions more usable for us all.

First we must understand about relaxation and creep.

5.1 Relaxation and creep



When you apply a sudden, fixed strain to a sample it will start to relax and the measured stress will decrease. The image shows a typical plot of stress σ over time. If the initial strain had been doubled, the initial stress would also have been doubled. So you also see equivalent plots of Relaxation Modulus G=σ/strain. Such plots are Relaxation curves.



If you apply a fixed stress to a sample, it will suddenly start to creep, i.e. the strain increases. The image shows a typical plot of strain (here shown as ε for historical reasons) over time. If the initial stress had been doubled the resulting strains would double. So you also see equivalent plots of Compliance J=strain/σ. Such plots are Compliance curves.

You would think that looking at stress for constant strain and strain for constant stress would be highly inter-related - and they are. However, in just about every reference I could find, they were discussed via entirely different equations, implying that they are totally unrelated.

Relaxation is typically modelled using a Maxwell model:

Equ. 5-1
$$\frac{\delta\gamma}{\delta t}=\frac{\sigma}{\eta}+\frac{1}{E}\frac{\delta\sigma}{\delta t}$$

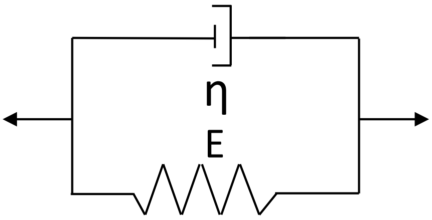
What this tells us is that the rate of change of stress with time (which is what interests us) depends on the modulus (here we use the tensile modulus E but this could equally be the shear modulus G) and on the ratio of the current stress σ to the "viscosity" η. It also depends on the change of strain, γ, with time.

As we are only interested here in an instantaneous step change in strain, the equation simplifies to stress having an exponential decay time depending on E and η. The elastic and viscous components are coupled in series, shown as a spring and dashpot. Any real material (and this is a key part of this chapter) cannot be modelled with a single pair of E and η values. The relaxation process involves multiple aspects of the material over different timescales. So the representation of a real system requires a set of different E and η pairs which (because η is in Pa.s) give responses at different timescales. We will return to this later.

Creep is typically shown via the Kelvin-Voigt model:

Equu. 5-2 $$\frac{\delta\gamma}{\delta t}=\frac{1}{\eta}\left(\sigma-E\gamma\right)$$

As with Maxwell, we are interested in the response to a sudden increase to a constant stress, σ, and again we end up with an exponential depending on E and η.

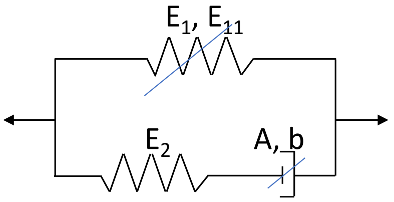


The model is now a spring and dashpot in parallel and, as for relaxation, the compliance curve for real materials requires a set of different E and η values working over different timescales.

Although there are clear similarities between the two models and how they are used, they are each useless for describing the behaviour of the other model - they simply give nothing like a realistic response. So although *all* materials have complex relaxation and creep behaviours, these two standard models used throughout the rheology world are incapable of producing the real-world behaviour. So if you want to know, approximately, how a material with a given modulus and viscosity might behave under various relaxation and creep scenarios, the assumption throughout the rheology literature is that you have to build two separate models and make what you can of them. I find that completely unacceptable.

After some searching through the literature I found some papers[12] that let us see both behaviours with a single set of inputs. There are plenty of rheology experts out there writing plenty of books and guides; why was it so hard to find a model that unifies two key aspects of rheological behaviour?

Those interested in the formulae can find them in the app (or the original papers). The key is the model being used:



We now have two springs. E_1 is a strain hardening spring (hardened by factor E_{11}) which means that the more it stretches the harder it becomes. And the dashpot is non-linear depending on a frequency component A and a non-linearity component b which, when 0 gives a conventional dashpot with A becoming η. Both non-linear aspects are typical of most polymer-based formulations, especially those with some degree of cross-linking.

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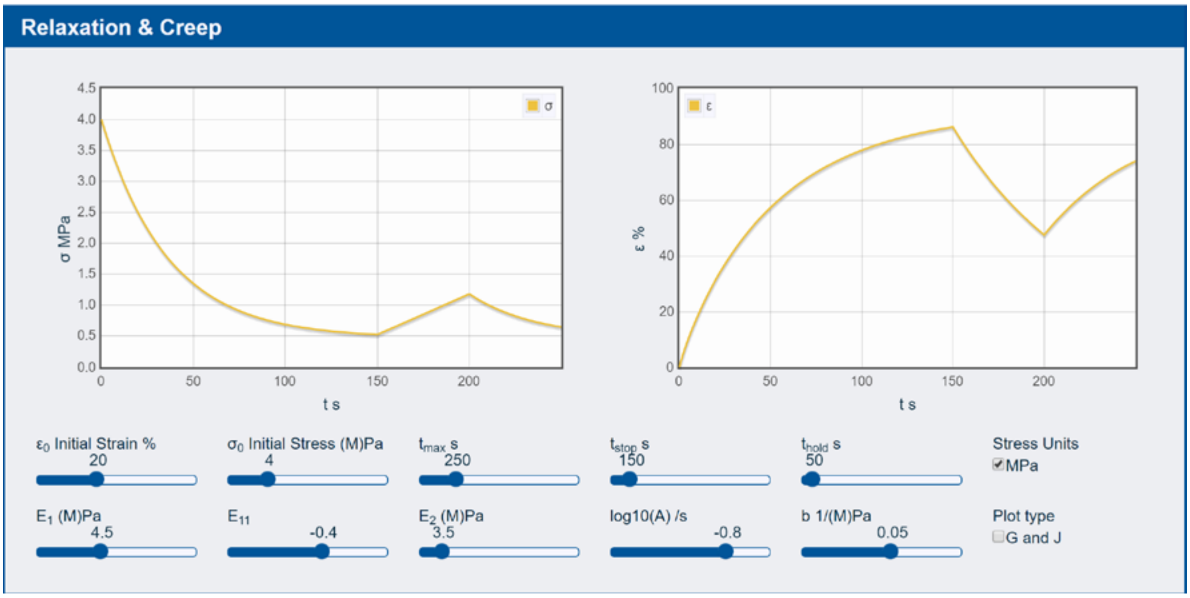
[12] Antonios Zacharatos, Evagelia Kontou, *Nonlinear viscoelastic modeling of soft polymers*, J. Appl. Polym. Sci. 2015, DOI: 10.1002/APP.42141, Rui Miranda Guedes1, Anurag Singh and Viviana Pinto, *Viscoelastic Modelling of Creep and Stress Relaxation Behaviour in PLA-PCL Fibres*, Fibers and Polymers 2017, 18, 2443-2453



ε_0 Initial Strain % 20

σ_0 Initial Stress (M)Pa 4

t_{max} s 250

t_{stop} s 150

t_{hold} s 50

Stress Units ☑ MPa

E_1 (M)Pa 4.5

E_{11} -0.4

E_2 (M)Pa 3.5

log10(A) /s -0.8

b 1/(M)Pa 0.05

Plot type ☐ G and J

App 5-1 https://www.stevenabbott.co.uk/practical-rheology/Relaxation-Creep.php

We can now play with the various stresses and strains, timescales and spring and dashpot parameters. Because such experiments are carried out on relatively fluid materials using low stresses in the Pa range and on semi-solids with stresses in the MPa range, you can choose the units - these merely change the graph labels.

As mentioned at the start of the book, I am being inconsistent: strains are shown as ε rather than γ. In this sort of plot it would be odd to use γ. As I said at the start, rheology is full of inconsistent units.

The curious shape of the curves comes because after 150s (see the t_{stop} slider) the strain or stress is reduced to zero and the system starts to return to its original value via its elastic response though clearly it will never fully return because the viscous component is irreversible. After 50s, (t_{hold}) the stress is re-applied and the strain or stress increases further. Such experiments are very much part of the repertoire of relaxation and creep measurements, though I currently have no idea how you use the data from multiple starts and stops.

Earlier I said that all real-world relaxation and compliance curves can be described with a series of Maxwell or Kelvin-Voigt G:η pairs. The app has bypassed this by using more complex springs and dashpots. In reality the stress/strain-dependent elements could have been emulated via a series of pairs. This fact will be key to the discussions in the next section.

As mentioned above, if the relaxation experiment is done with a different strain, then the recorded stress will be different. For example, doubling the strain will double the stress. Similarly, if the creep experiment starts with double the stress then the strains will double. If you need to compare samples measured at different strains or stresses, just looking at the plots will be unhelpful. We can solve this problem. Instead of plotting σ we can plot σ/ε, as G(τ) the Relaxation Modulus at any given timescale τ in units of Pa which will give Relaxation curves that are identical over a reasonable range of strains. And instead of ε we can plot ε/σ, as J(τ), the Compliance in units of 1/Pa and the Compliance curves, again, will be identical over a reasonable range of stresses. Using G(τ) or J(τ) curves we can therefore make meaningful comparison between samples which might have been measured at different strains or stresses.

What happens when linearity of response breaks down is discussed in a very brief chapter.

These two plots are based on elastic and viscous components. So they must be related somehow to G' and G''. The timescales in the screenshot are in the 100s range, so 0.01HZ. A typical oscillatory measurement of G' and G'' takes place in the 0.01 to 10Hz range, So these data should have some links to low frequency values. If we did a much slower creep test (and why not?) maybe we could get G':G'' data in the super-low frequency range. If we wished to know about relaxation and creep behaviour in the 0.1s timescale (which is tricky because the assumption of "instant" stress or strain becomes difficult to justify) we could, perhaps, use the 10Hz G':G'' data.

5.2 The power of interconversions

As mentioned above, all real-world relaxation curves are constructed from G:η pairs that work over different time-scales. If we happen to know all such pairs across the whole time domain then we can plot the relaxation modulus, G(τ) , for all times from microseconds to macroseconds. We also know that all G':G'' measurements are frequency dependent. It would be rather helpful to see which are the frequencies where "interesting" things happen and which are those where there is not too much of interest.

If we had such a plot of "interest" versus frequency we could then think through the timescales of the processes that are important to our formulation and know with confidence that our system has the chance of giving the correct response. What does "interesting" mean, and what would be the correct response? Only you can answer those questions - it is your product, not mine.

My shock at learning that such a plot was possible and (in theory at least) routine, was mostly to do with the fact that because I had been unaware that such a thing could be done, I had never asked myself the sorts of questions that the technique would have answered. If I had known, for example, that a rapid change was taking place at a timescale important to my process, I would have been alerted to the process being on a knife-edge and could have devised methods to shift the peak to a different timescale.

The plot of H (representing the degree of interest) versus t is called the *relaxation spectrum*. I hope, therefore, that you will take the trouble to learn about H (and its equivalent in terms of creep is the compliance spectrum, L), and find out how to obtain them.

Before looking at relaxation spectra we need to think more about creep-style measurements. The compliance curve, the creep strain experiment normalised by the applied strain, can, just like the relaxation curve, be defined by a series of G:η pairs. We could also, had we been interested, determined J' and J", the storage and loss compliances. In simple terms, these are measured via the strain response (creep) to an oscillating stress. The interrelationship is simple because G'/G" = J'/J" and a modest bit of algebra creates the full interconversion. This means that whether you have a constant stress or constant strain measurement technique, you can always output G':G" or J':J" according to your needs.

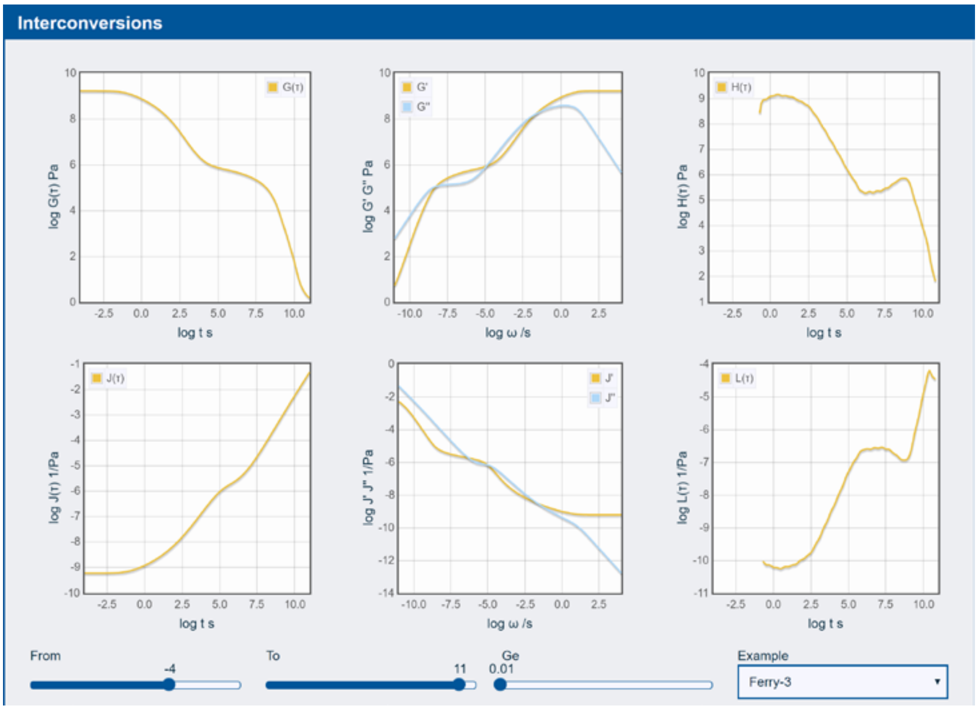
And if we can imagine a relaxation spectrum we can imagine a compliance spectrum.

So far we have four properties that can be derived and which are clearly inter-related. The final two properties are the relaxation and compliance spectra.

If you say that the relaxation modulus is derived from a set of G:η pairs then we need some coefficients to say how much of each of them is to be included in the overall modulus. Because G:η defines a timescale, what we need is a coefficient for each component at each timescale. This set of components is the relaxation spectrum when it applies to relaxation curves and the compliance spectrum when applied to compliance curves. The beauty of these spectra is that at a glance you can see at which timescale(s) interesting things happen. Any peak or trough in the spectrum alerts you to something interesting happening at that point. If your process timescales are at those points that means that relatively small changes in the process will have a relatively large effect on performance.

So we should always have access to our relaxation or compliance spectra. Except that we don't, because (a) most of us never knew that they existed and (b) determining these spectra requires measurements over many timescales and, in general, we are good only at looking at processes over rather limited ranges, such as the 0.01 to 10Hz of a G':G" measurement.

I cannot tell you how to do this in practice. All I can do is show you what the world would be like if we could readily interconvert between all six ways of looking at the data. As mentioned above, most papers on interconversions are either inscrutable (to me) or offer only a subset of conversions. In the end I was able to assemble a good-enough collection of algorithms by combining Ferry, Tschoegl and Park.[13]



From -4

To 11

Ge 0.01

Example Ferry-3

App 5-2 https://www.stevenabbott.co.uk/practical-rheology/Interconversions.php

What the screen shot doesn't show is the rather messy method for creating the inputs - a series of G(τ) values at different timescales, i.e. the relaxation modulus curve at the top left. This is often called a Prony series. From this the other five curves are calculated via a set of rather tricky calculations that I managed to extract from the literature after a great deal of difficulty.

Ferry's book contains eight examples that cover a wide range of behaviours and by selecting each option you get a rather good guide through the types of behaviour you are likely to find, at least in the world of polymers. My way of testing the app was to compare the results to Ferry's. Within the limitations of reading data off some digitized images of Ferry's printed plots, the matches are adequate.

For me the key curves are the relaxation and compliance spectra on the right-hand-side. They convey so much information about the timescales of the processes involved and, again, by flipping through the Ferry datasets you will start to build up an intuition about what the spectra mean and how useful they would be if we could routinely obtain them.

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[13] John Ferry, *Viscoelastic Properties of Polymers* 3rd Edition, John Wiley, 1980; Nicholas Tschoegl, *The Phenomenological Theory of Linear Viscoelastic Behavior,* Springer, 1989; SW Park and RA Schapery, *Methods of interconversion between linear viscoelastic material functions: Part I a numerical method based on Prony series*, International Journal of Solids and Structures 36, 1999, 1653-1675.

Because compliance is, at heart, just 1/relaxation, it is not surprising that the curves look somewhat like mirror images. If it were that simple then life would be much easier. In fact the conversions are not at all straightforward and the curves, at the detail level, are not mirror images.

Some of the curves have calculation artefacts. That is partly a limitation of the algorithms I used and also a characteristic of the problem of these conversions. I have the advantage of data from Ferry, covering many orders of magnitude of timescale, which makes it possible to show the full conversion capabilities. In real life you will have only a limited set of data unless you do extensive WLF conversions. The fewer the number of datapoints, the more likely the conversions will contain artefacts. As many papers stress, some of these conversions are "ill-posed problems" which means that there is no unique solution.

Out of personal interest I attempted to create the interconversions for the Burgers model shown in the previous chapter and discussed further below. You can judge my attempt by selecting the option from the combo box. Although I can convert from a series of G(τ) values to G':G" I don't have a method to go in the other direction so that we could take any G':G" dataset and create the full interconversions. To get these G(τ) values I used trial and error. Automating the G':G" conversion may be a future challenge.

The difficulties of interconversion might make it hard to realise my dream scenario which is the ability to combine data from whichever techniques happen to be convenient for different timescales. Perhaps this has already been done by some smart academic who has then hidden the technique behind a wall of Laplace transforms[14] and triple integrals. That simply is not acceptable. This is the 21st century; modern programming languages are so easy that even academics can write using them. It hardly matters which language is chosen because they are approximately all the same: I have created apps in Javascript by converting from C, BasicA (that's really, really ancient Basic running under DOS), Fortran, Pascal and Mathcad. If I can do it, so can anyone.

5.3 Entanglement

In the viscosity chapter I spent time talking about entanglement as a key aspect of formulations. With viscosity measurements, entanglement is related to the concentration where viscosity starts to increase rapidly. This is important in the solution phase of a formulation. It doesn't help with understanding the properties of the final semi-solid, such as pressure sensitive adhesives (PSA), because rotational viscosity doesn't work on them. I will use the world of PSAs to show

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[14] Chapter 4 of the excellent *Rheology for Chemists* by Jim Goodwin and Roy Hughes is an example where the intentions are good - the authors are also passionate about explaining to chemists such as myself how interconversions can provide powerful understanding. Yet the "simple" idea of a "functional" to help these conversions is described via a Laplace transform. A further simplification takes us to the Dirac delta function. The trouble is that most of us who read the chapter can do nothing with these ideas.

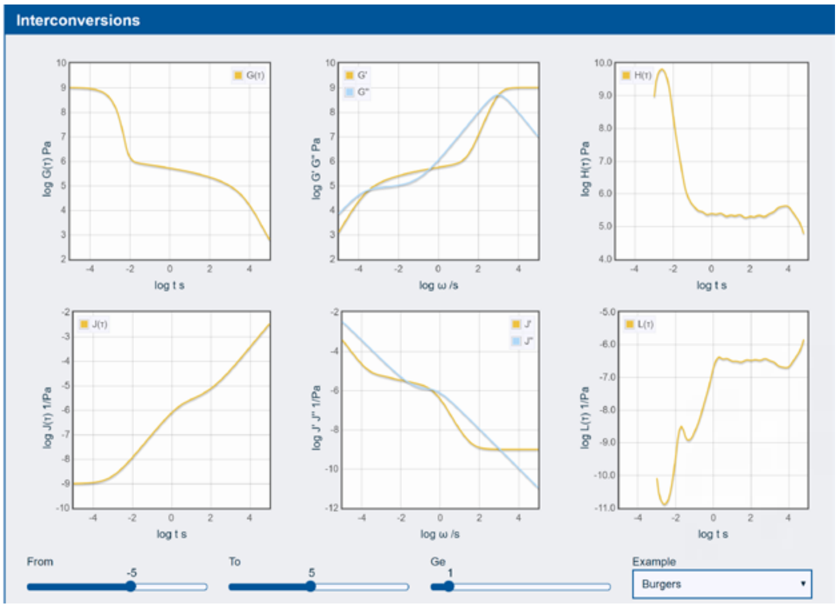
why interconversion is so important, simply because I know a lot about them and already have a good model for what they should be like. If I had more experience in other areas I could equally have used them as examples because the principles are general. Macosko's *Rheology Principles* book is especially good for those who want to explore other implications of entanglement.

The common idea of a strong adhesive (such as an epoxy) is that it gets its strength from having a high elastic modulus. A polymer with lots of entanglement (such as a cross-linked epoxy) will behave as a pure G' over the normal timescales that we typically measure. Such a polymer would make a useless PSA because these have to be soft and accommodating to the surface - they must have a G' no larger than 0.3MPa, compared to a typical epoxy's 4GPa.

Any polymer without entanglement is going to behave with a large G'' element as there is nothing much to stop the polymer chains from sliding past each other. A PSA without tangles might still achieve the 0.3MPa G', while having a G'' significantly higher. As an adhesive it will be useless because it won't absorb any energy (that's what the elastic component does) and will just allow a facile failure.

The PSA, therefore, needs to have the right blend of entangled and non-entangled polymer, where "right" applies to the timescales of interest. As discussed in the Semi-Solids chapter, the key test of adhesion is normally done at ~100 /s, the ability to create a tacky adhesive force needs to take place over the ~1 /s timescale and creep is usually a concern around the 0.01 /s timescale. [For more on this, see the Chang Window app at https://www.stevenabbott.co.uk/practical-adhesion/chang.php.] To get an overview of any formulation we therefore need to see things from the 10^{-3} to 10^{3}s timescale, though if we are worried about low and high temperatures we probably need 10^{-4} to 10^{4}s. Whether this is best done via a full WLF set of G':G'' data or whether it could be stitched together with some, say, creep tests and some relaxation tests I cannot say. [One type of creep test that is especially useful for PSA, and which links directly to the Burgers model discussed earlier is described as the "small strain shear test", which rheologists will recognize using a different terminology: https://www.stevenabbott.co.uk/practical-adhesion/psa-shear.php.] What I can say is that if we had a full interconversion set for a typical PSA we would be able to make those decisions more rationally.

Because the default settings of the Burgers Viscoelasticity app are (by no coincidence) representative of a typical PSA, as mentioned above, I created a relaxation modulus dataset which is included in the Interconversions combobox.



From: -5
To: 5
Ge: 1
Example: Burgers

Figure 5-1 The Burgers Viscoelastic model for a PSA fully interconverted

What I especially like about this interconversion is the ability to think better about creep behaviour. It is rather easy to design an excellent PSA which fails in the application because of creep. The standard "creep" test is simply "how long does it take for this sample to fall from the test rig", providing very little information about what is going on. The interconverted creep curves allow me to think more about the timescales over which creep will be a liability. If the PSA world routinely looked at creep this way, it would be much more knowledgeable than it currently is.

5.4 M_c from Likhtman-McLeish theory

Suppose you have a full G', G" curve covering many orders of magnitude. There is one more thing you can do with it - work out the critical entanglement molecular weight M_c. The theory was developed by Likhtman and McLeish[15] some years ago, but most of us were totally unaware of it because it's the sort of thing known in the specialist M_c community, not among those of us who need it. An appified version, https://www.stevenabbott.co.uk/practical-rheology/L-M_Mc.php, was made possible by the kind assistance (acknowledged on the app page) of those who are supporting and developing this, and other theories for the future. Indeed, they have provided L-M theory as part of the impressive RepTate software (https://reptate.readthedocs.io/) which does a better job than my app - and provides alternatives for those who want a more advanced fit.

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[15] Alexei E. Likhtman and Tom C. B. McLeish, *Quantitative Theory for Linear Dynamics of Linear Entangled Polymers*, Macromolecules 2002, 35, 6332-6343

Mwt (k) 100

Z=Mwt/Me 20

τ_e µs 6

G_e factor 1

c_v 0.1

Polymer PCL

T °C 60

Me --> Mc 5000 --> 10000

G_e MPa 0.6

τ_R ms 2.4

Load local file No file chosen

Figure 5-2 The Likhtman-McLeish route to finding M_c values.

The app is mentioned here because L-M theory provides us with two key outputs - the M_c itself and a Rouse relaxation time, τ_R. That relaxation time is based on on input value, τ_e, which is the entanglement timescale. The other inputs are MWt of the polymer being measured and Z, the number of entanglements per that MWt. What the app does is take those 3 inputs and calculates the G':G" curves. What you do is move the sliders till the calculated and experimental values are a good-enough match. Although it would be possible to add an automated fitting, I find it more instructive for the user to see the trade-offs between the different possibilities. There is an extra fudge factor (it shouldn't be needed, but the experts recommended it) to adjust the maximum G' value, G_e. This makes the fitting easier.

The paper itself isn't so hard to read and the formulae not so hard to understand. Unfortunately one of the formulae is near-impossible to calculate. So in the app I make use of (as does RepTate) some heroic pre-calculations of curves depending on all (relevant) possible input values. The app, therefore, is not doing any calculations, just showing the curves expected from the current parameters. This means that we have a very powerful app without the need for vast computational power.

The science behind the app can be described very briefly. The high-frequency G' depends only on the number of entanglements - the more entangled, the higher the modulus. The low-frequency effects depend on τ_e, because, as we know from the interconversions discussion, relaxation times are related intimately to the other possible curves.

If (big if) you have a polymer with a low polydispersity index (<1.1) and if (big if) you have a full WLF set of G':G" data then the fitting is easy and if (big if) you have the WLF data corrected for a temperature that is a reasonable balance between T_g and T_m the results are sound. Most of us, most of the time, have polydisperse polymers so what should we do? The purist answer is to wait till some newer, better theories are available (and added to RepTate). My answer is to be pragmatic and get at least a working idea of what's going on with your polymer via a pragmatic M_c.

5.5 Impossible interconversions?

The book started in the familiar world of rotational viscosity, where we can go from shear rates of 0.01 to 10,000 with no great difficulty. It seemed obvious to me that there was one more interconversion we needed - taking the rotational viscosity data and using it to fill out tricky parts of the six interconversions.

I realised that I had never come across such a conversion methodology and was rather mad at myself for having missed something so important. I then did a literature search and came up blank. Then I asked a rheologist guru how to do it. He laughed and told me that not only was it impossible but that a further conversion, from extensional viscosity was also impossible - indeed, it often wasn't possible to convert extensional viscosity results between different ways of measuring the same material. This point is nicely described in the opening of the abstract of a famous paper[16]: *"The issue of whether extensional viscosity is a concept that causes more confusion than enlightenment is addressed".* The conclusion of the paper is that extensional viscosity causes plenty of confusion and that reducing the confusion looks to be a difficult task.

I will say no more about extensional viscosity other than to express my regret that a technique which should be so relevant to so many formulation issues remains unfamiliar to most of us and, apparently, so difficult to master.

I am genuinely astonished that after decades of rheological studies, there is (apparently) no methodology for combining rotational and oscillatory rheology. Readers will say "What about the Cox-Merz rule?" The answer is that it is not a rule and if it applies at all it is to a rather narrow domain (and does *not* apply at all to particle systems[17]). Cox-Merz says that the viscosity, η, at a given shear rate is equal to the complex viscosity, η*, when measured at the equivalent frequency, ω. As a reminder, G* is the complex modulus and the complex viscosity is given by $\eta^* = G^*.\omega$. There are at least two reasons why Cox-Merz is not a rule. First, there is no theoretical reason why it should be the case (i.e.

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[16] Christopher J.S. Petrie, *Extensional viscosity: A critical discussion*, J. Non-Newtonian Fluid Mech., 2006, 137, 15–23

[17] For those who are comfortable with "shear stress equivalent inner shear rate", Cox-Merz can be applied to particulate systems. I confess to not having the slightest idea what that phrase means. Those who are interested can find the ideas in the work of Prof Gleissle in Karlsruhe.

you cannot derive it from first principles). Second, η is a real number and η* is a complex number - you cannot just declare them as being equal.

5.6 What can we do with interconversions?

My view is that the ability to convert between (at least) the six views of the same data is of huge importance, that it is just about possible and that, despite numerous academic papers, this ability is very little understood and used. Also the potential for combining values from different techniques is enormous yet has been, as far as I can tell, hardly used. In addition we have extensional viscosity which isn't even self-consistent within itself. And we have rotational and oscillatory techniques, the twin pillars of rheology, that have no way to communicate with each other.

This means that the current answer to the question of what to do with interconversions is "not much".

If I were a rheologist I would see this as the grandest of grand challenges. Whoever could bring all those things together into a workable tool would transform our ability to better understand our systems via a series of systematic measurements.

So despite being at times rather critical of rheologists, I shall end this chapter on that positive note: maybe someone will take up the challenge, gain justified accolades, get the approach appified, and everyone will be much better off. Or, at the very least, the chapter might have encouraged some readers to go to the little-used Interconversions portion of their rheometer software to see what it can do for them.

6 Beyond linearity

What problems are we trying to solve?

Our rheology experiments are performed rather gently so we do not end up in "non-linear" domains where the standard analysis tools fail. Our real world formulations often operate within non-linear domains so ideally we would routinely be experimenting in these wilder areas.

This is a very, very short chapter.

Our real-world formulations are likely to be subjected to large stresses and strains. Yet our rheological measurements generally stay in a comfortable range of small stresses and strains - for good reason. The theories make sense within small stresses and strains where the elastic response is linear. The G' and G'' analyses that we use most often are very clearly limited to small strains so any standard analysis falls apart when the amplitudes get large enough to represent real-world stresses and strains.

6.1 LAOS

Most modern rheometers can now carry out Large Amplitude Oscillatory Shear (LAOS) measurements. With a few Lisajou figures and Fourier transforms, a lot of interesting information becomes available. In planning this guide I asked a rheologist guru how much effort I should put in to understanding and explaining LAOS. His reply was clear: "Don't bother. It is early days, it is very tricky, and you and your readers already have enough problems with standard rheology". I am happy to accept that advice.

Because it is clearly a technique of great potential importance, I urge readers to get the friendliest-possible introduction via Prof Gareth McKinley's brilliant TA Instruments webinar at https://www.youtube.com/watch?v=LtoRnBt70wM. I had to use the pause and rewind buttons many times to keep up with the flow of exciting ideas, so make sure you have some quality time to spare if you want to dive in.

If a LAOS expert thinks that this chapter should be greatly expanded, to allow the technique to be explained to a wider audience, I would be delighted to work with them to make it happen.

7 Particle rheology

What problems are we trying to solve?

We already have the rheological methods that apply just as much to particulate systems as to others such as polymers. The problems of interest here are how to related rheology to particle properties or, conversely, how to formulate our particles to obtain the rheology we require - especially obtaining the lowest possible viscosity at the highest possible particle concentration.

There are two big areas of rheological interest for particles. The first is the low shear and yield stress domain. The second is the high shear domain. Clearly the high shear domain builds on key parameters from the low shear domain, so we start with that once we clear up the issue of what constitutes a particle.

There are at least three areas of particle rheology: solid particles, emulsions and foams. Much of the rheology of emulsions follows the scheme discussed in this chapter. The main difference is that because the particles are deformable, the high-volume fraction behaviour is, in one way, more forgiving. The trouble is that high-volume fraction emulsions have the tendency to invert, becoming a low volume fraction emulsion. So a 70:30 oil-in-water emulsion might (and often does) invert to a 30:70 water-in-oil emulsion. Those who want to know more can read about it in my Practical Surfactants website, https://www.stevenabbott.co.uk/practical-surfactants/, and the free eBook downloadable from that site.

The rheology of foams also follows some of the general rules, with yield stress being especially important for cosmetic, pharma and fire-fighting foams and the shear thinning behaviour is also important for fire-fighting[18]. The low-shear behaviour is described in foam apps within the Practical Surfactant website.

Having put two major, related areas of particle rheology to one side, we can return to our main themes involving conventional solid particles.

7.1 Low Shear and Yield Stress

Everyone spends time with Einstein and Taylor expressions for the effects of particles on low shear viscosity. As these are hopelessly wrong for any interesting volume fraction, φ, I will be an exception and go straight to the key general expression and discuss a few variants which seem to me to be largely irrelevant though they excite a lot of discussions.

The discussions will first be about spherical particles.

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[18] At the time of writing I am working on a project to predict the behaviour of fire-fighting foam flowing down pipes on big oil installations. The "particle" nature of foam is especially important in the theory, with the added complication of the compressibility of the foam particles.

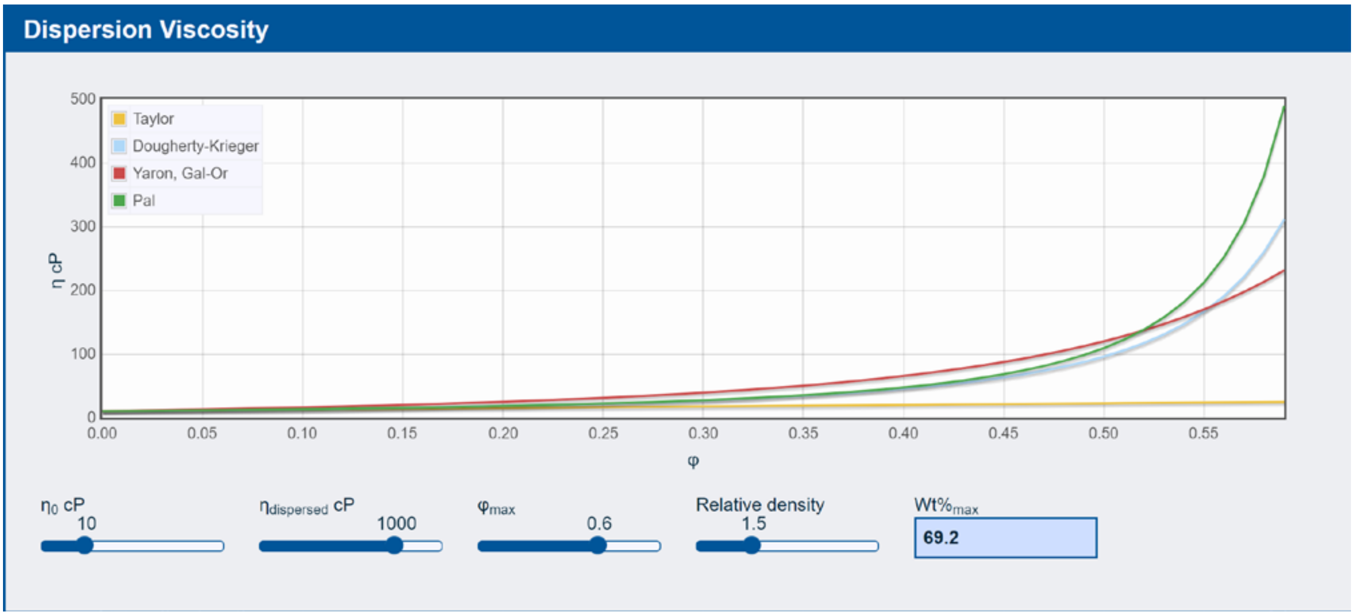
The key is that for particles there is a maximum volume fraction, φ_m called the packing fraction at which point the system is effectively a solid. The frequent big debates about the precise value of φ_m are missing the point. Few of us[19] know our real φ_m values as our formulations are not perfect spheres. The point is that all formulations have a φ_m and we can either stay far away from it so that small changes in φ_m make little difference, or we adopt a few tricks to change it to a higher value to keep viscosities and yield stresses as low as possible.

The most common equation for describing the effect of φ is Dougherty-Krieger. Others, such as the one from Pal, may or may not be superior in some ways, but again it hardly matters for our real-world formulations of imperfect particles:

Equ. 7-1

$$\eta = \eta_0 \left(1 - \frac{\varphi}{\varphi_m}\right)^{-2.5\varphi_m}$$

The important point is that as φ approaches φ_m the viscosity goes to infinity, as the app demonstrates:



η_0 cP 10

$\eta_{dispersed}$ cP 1000

φ_{max} 0.6

Relative density 1.5

Wt%$_{max}$ 69.2

App 7-1 https://www.stevenabbott.co.uk/practical--rheology/Low-Shear-Particles.php

This is all a great simplification. Values of φ between ~0.47 and 0.58 give a phase separated state which many of us have never noticed as it seems to require careful measurement with nicely spherical particles to observe it. In practice this means that φ_m is more likely to be 0.58 than 0.63. Other data tell us that φ_m is shear rate dependent.

Before describing the method of increasing φ_m let us first look at yield stress.

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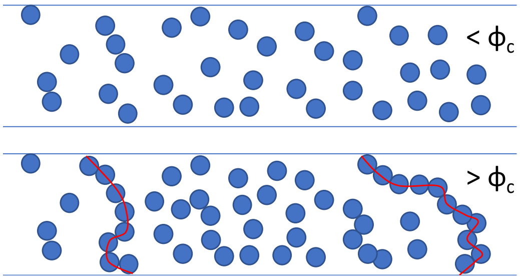
[19] If you are very keen you can squeeze a particulate slurry with some sort of filter beneath it and wait for it to become solid. If you can then weigh the solidified form then extract the liquid and re-weigh you can measure the packing fraction.

7.1.1 Yield stress

Because yield stress is so hard to measure unambiguously, and because theories apply more to perfect spherical systems, we need only a "good enough" theory to know what factors influence it so we can control them as best we can. I have chosen Flatt and Bowen's YODEL[20,21] theory because a simplified version works well in an app and those who want more complexity can go straight to the authors' papers if they wish to be more sophisticated.



First we need to introduce φ_c which is the critical percolation threshold. To explain this, imagine that you have some soil or rocks with spherical holes in it, with water beneath and dry ground above. If you have just a few holes, there is no guaranteed path taking the water from hole to hole through to the surface. As you increase the number of holes, the water still cannot percolate through. At φ_c there are sufficient holes for a path for the water to be statistically likely to percolate through; this is the percolation threshold. Now make those holes into spheres. Below φ_c there is no continuous particle-to-particle network across the sample, so motion is relatively free. Above φ_c there is a network of touching particles so movement of the particles is greatly restricted. For spherical particles this is at φ=0.28. As particles acquire a greater length to width ratio (aspect ratio) it becomes easer to find a percolation route. One of my apps shows this: https://www.stevenabbott.co.uk/practical-coatings/percolation.php. When the aspect ratio is ~100, you need only 0.7% to get percolation - which is another way of saying that a dispersion of just a few % of carbon nanotubes will have a high yield strength[22].

My simplification of YODEL says that:

Equ. 7-2
$$\sigma_y = k\frac{E}{r}\varphi\frac{(\varphi-\varphi_c)^2}{\varphi_m(\varphi_m-\varphi)}$$

E is an interaction energy in units of kT, where, as DLVO theory[23] tells us, this might be something like 3 or 4 for a lightly flocculating system[24]. Well-dispersed

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[20] Robert J Flatt and Paul Bowden, *Yodel: A Yield Stress Model for Suspensions,* J. Am. Ceram. Soc., 90, 1038–1044, 2007

[21] Although YODEL stands for Yield-stress mODEL, it is not a coincidence that the authors are Swiss

[22] An app that calculates φ_c is at https://www.stevenabbott.co.uk/practical-coatings/percolation.php. For those who wish to make a conducting material, guaranteed conductive path for the electrons to travel conduction only happens above the percolation threshold. An approximately spherical particle such carbon black needs 28% to make the material conductive. If you use the currently fashionable silver nanowires, just a few % is all you need.

[23] An app in my Practical Solubility site helps explain this for those who want to know more: https://www.stevenabbott.co.uk/practical-solubility/dlvo.php

[24] Alert readers will say that E is -3kT for a flocculating system. I just find negative signs in equations confusion.

systems in the 2-3 range give lower yield stresses than systems with bad dispersants in the 8-10 range. The particle radius is r, with smaller particles, other things being equal, giving a higher yield strength as our instincts tell us. The constant k is my fudge value to provide plausible results. A screenshot of the relevant app follows shortly because it is incorporated into the high-shear app thanks to the commonality of many of the key inputs and calculations.

Although the effects of the interaction energy and radius are important (proportional to E and 1/r respectively) the biggest effect is the rapid rise with φ as it starts to approach φ_m. So paying attention to small changes in φ can be more rewarding than worrying too much about E or the meaning of r in a system with a range of particle sizes. If φ_m is a given then E becomes important. The aim of "super-plasicizers" in cement is to reduce E so the cement has the maximum flowability with the least amount of water. I had always imagined cement to be a rather boring product; reading the work of Bowen's group soon dispels that idea; indeed, a lot of the cutting edge rheological work on particulate system comes from the cement industry.

7.1.2 Microrheology

I was visiting the lab of an expert rheologist and we discussed many of the classic issues of rheometers for particle-based systems. He then pointed out that microrheology was a neat rheometry technique that used the particles themselves. I don't know who was the more surprised: him that I'd never heard of microrheology, or me that such a wonderful technique existed.

The basic, passive, technique is to look down a microscope at your particles and track their random motion over time. As the particles get larger and/or the viscosity gets higher, the technique gets less and less useful as the random motions are so small. The more advanced technique is to drive the particles with an active field (e.g. magnetic or laser tweezers) in a known oscillation mode. The response of the particle to the oscillating field can then be analysed (in exactly the standard G':G" method reflecting the in-phase and 90° components) and the rheological properties worked out. With a sophisticated system it is possible to apply significant forces that allow measurements of, e.g. creep and recovery.

The classic technique adds tracer particle probes to a fluid. For particulate systems the many particles help to solve a specific problem of the basic, passive technique. It is possible that any single particle might be stuck in some local environment that doesn't represent the whole. By tracking multiple particles and by correlating their motions, a fuller picture of the rheology can be obtained.

My understanding is that it is a relatively specialised technique that is certainly not routine. I include it here for those who, like me, had never come across it before.

7.2 High Shear

We know that viscosity goes to high levels at low shear and high φ. This would mean that high-solids formulations would be impossible to handle. Fortunately, they shear-thin strongly, though caution is required because at very high shear rates some formulations can shear thicken alarmingly.

The theory I've chosen[25] has, not surprisingly, many elements that are common to the many alternative theories found in the literature. It is especially useful for an app because it relies mainly on just two inputs which we already know: φ_m and φ_c. The key equations are:

Equ. 7-3

$$\eta = \dot{\gamma}^{n-1} \text{ and } n = \frac{\left(\frac{\varphi}{\varphi_m}\right)^{2/3} - 1}{\left(\frac{\varphi_c}{\varphi_m}\right)^{2/3} - 1}$$

Other elements of the equation are described in the app - which we need because it is hard to grasp what such an equation will produce. The results turn out to be rather straightforward, at least when viewed as a log plot:

φ_c Percolation 0.28

φ_m Packing 0.63

N 1

Fractal Dim. d 3

Aspect Ratio A_f 1

φ^* : $\varphi_{c\ calc}$ 0.63 : 0.285

☑ Log(γ̇)
☐ Log Normal

● Viscosity
○ Stress

☐ High γ̇ Corr.
☐ Shear Thicken

λ Size ratio 1

k Fraction Small 0.33

φ_{max}Bimodal 0.63

E in kT 9.3

r radius nm 2060

φ_{max} 0.45

App 7-2 https://www.stevenabbott.co.uk/practical-rheology/High-Shear-Particles.php

The starting point is spherical particles with φ_c=0.28 and φ_m=0.63. As soon as you slide the Aspect Ratio slider, things start to change: φ_c goes down so both the yield stress and the viscosities go up. However, things are not quite that bad. If you turn on the high γ̇ correction then the high shear viscosities decrease sharply, especially for higher aspect ratios, as the particles can rather readily

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[25] Gregory A. Campbell, Michael E. Zak, Mark D. Wetzel, *Newtonian, power law, and infinite shear flow characteristics of concentrated slurries using percolation theory concepts*, Rheol Acta(2018) 57:197–21

slide past each other. The effect is modelled by increasing φ_m with shear rate, an effect well-validated in the literature.

If you decrease the Fractal Dimension from 3 (i.e. the system is no longer pure particles) and increase N, the number of particles in a floc, the viscosity increases sharply. How do you know the fractal dimension and the number of particles in a floc? In general we don't. The Bicerano paper[26] from which I extracted the relationship tells us that a platelet formulation has a dimension of 2, so any normally flocculated system will be something like 2.5, which is the default used in some of the graphs in that paper. In terms of N, you have to decide whether the shear stresses at a high N value are likely to rip the flocculated particles apart or, as confusingly happens, makes further flocculation more likely as we will discuss shortly. To explore the effects, values of N from 2-5 seem to be reasonable.

Why do particulate systems shear thin so much? It is because the shear drives the particles into neat lines like vehicles flowing down the lanes of a highway rather than annoying lane-hopper motorists moving between lanes and causing everyone (including themselves) to slow down.

Why do some systems, after shear thinning as normal, shear thicken at very high shear rates. Think of this as a sort of Bernouilli effect where the air flow between the vehicles sucks them together, creating a massive pile-up: particles are structured across the rheometer gap, causing high viscosity. This is the transition from "hydrodynamic flow" to "lubrication dynamics" or "hydroclustering". There seems to be no convenient formula for this (and the effect is very formulation-dependent), so the Shear Thicken option merely illustrates the effect. This hydroclustering is discussed further in the shear thickening section.

7.2.1 Increasing φ_m

Even a small increase in φ_m can help with a high solids formulation. Increasing the aspect ratio makes this happen at high shear, with problems down at low shear thanks to the decrease in φ_c, so this is not a strategy to be encouraged, even if you could change the aspect ratio which, generally, you cannot.

Instead, the standard trick for our mostly-spherical formulations is to make sure that smaller particles in the formulation can fit in the holes created when the larger particles pack.

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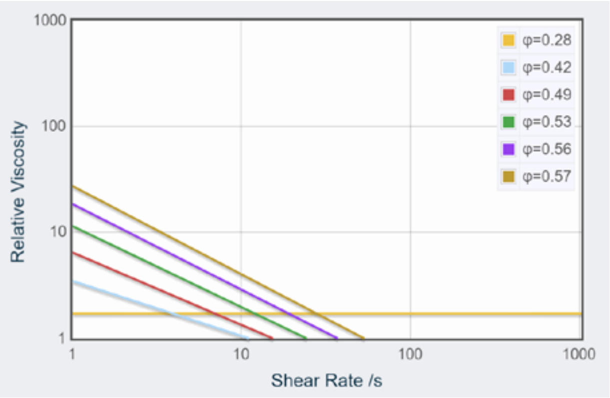
[26] Jozef Bicerano, Jack F. Douglas, and Douglas A. Brune, *Model for the Viscosity of Particle Dispersions*, Journal of Macromolecular Science, Part C, 39:4, 561-642



For a simple binary distribution it is well-known that there is an optimum size ratio and an optimum ratio of small to large particles. For a 10:1 size ratio with 33% of the smaller particles then φ_m goes from 0.63 to 0.7. If you make these changes to the app with unaltered values of φ_c and φ_m, you will see a large (20x) reduction in the viscosities, so such a modest change does make a significant difference.

Given that we tend to have polydispersed systems it would be good to be able to calculate φ_m for a more real-world distribution. I have not been able to work out how to do this[27]. In any case, such an ideal model would still have many assumptions, and, as hinted, the effective φ_m depends on shear rate - being closer to 0.5 at low shear and 0.7 at high shear. We can, though, take advantage of the fact that a log normal distribution with a standard deviation greater than 0.5 has a φ_m of 0.7. The explanation for this[28] is not, as most of us would imagine, that a broad distribution allows more small particles to fit into more big holes. I have so far failed to grasp the true explanation which seems to be about the fact that a wider distribution has plenty of larger particles that are more compact than the equivalent volume of smaller ones. In the app, the Log Normal option simply changes φ_m to 0.7.

The advice, therefore, is to keep particles relatively spherical, with a good dispersant and with a reasonable small:large ratio of particle sizes. You probably knew that already, but at least you now have some reasonable calculations available to you to see if the effort to improve the situation is likely to be worth it.

7.3 Particle Size Distributions

Discussions on viscosities of particle systems tend to focus, rightly, on volume fraction. There is the danger of over-focus because there are some important data hidden within the distribution curves. Let us look at some of the basics, then bring out those hidden data.

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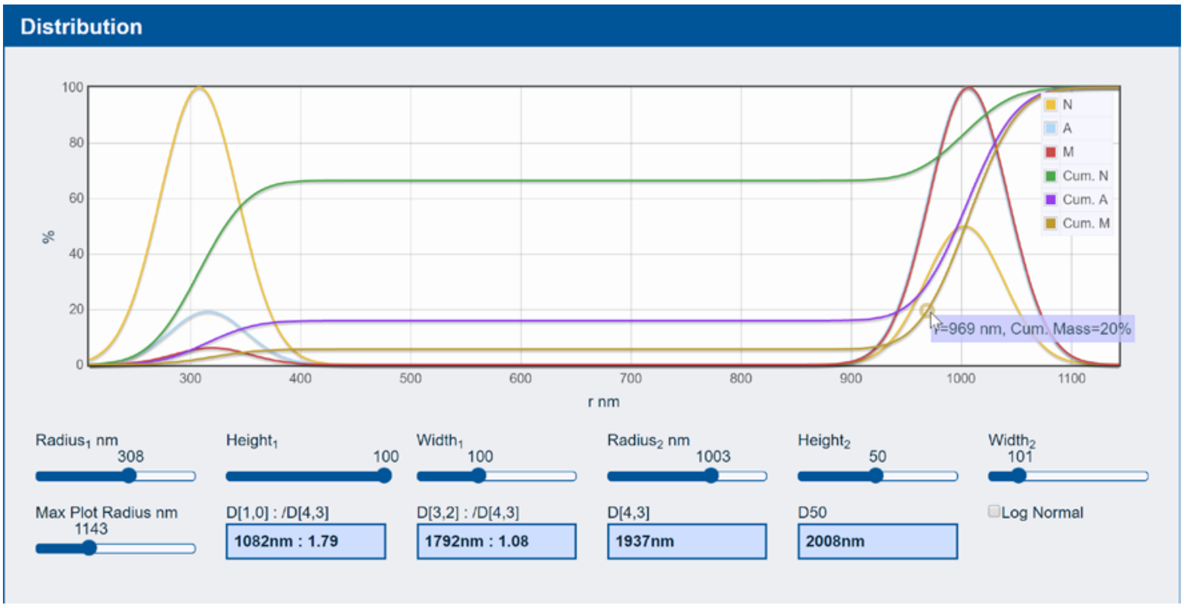
[27] The standard paper on this is from RJ Farris, *Prediction of the Viscosity of Multimodal Suspensions from Unimodal Viscosity Data*, Trans Soc Rheo, 12,281-301 (1968). Unfortunately I simply cannot understand it.

[28] G.T. Nolan and P.E. Kavanagh, *The size distribution of interstices in random packings of spheres*, Powder Technology, 78 (1994) 231-238



Radius$_1$ nm 308
Height$_1$ 100
Width$_1$ 100
Radius$_2$ nm 1003
Height$_2$ 50
Width$_2$ 101
Max Plot Radius nm 1143
D[1,0] : /D[4,3] 1082nm : 1.79
D[3,2] : /D[4,3] 1792nm : 1.08
D[4,3] 1937nm
D50 2008nm
☐ Log Normal

App 7-3 https://www.stevenabbott.co.uk/practical-rheology/distribution.php

Here we have a rather unlikely distribution, created only for visual convenience. We have a large number of 300nm particles and a set at 1000nm of half the number (the relative "Height" values are 100 and 50). They are the same 100nm nominal width. The yellow "N" for Number curve shows exactly what I have just described. The "Cum. N" curve shows the cumulative number and we find that 66% are below 400nm and 34% are above 900nm.

Now look at the M for Mass (or it could be V for Volume) curve. There is a tiny peak around 300nm and a huge one at 1000nm. The cumulative curve tells us that only 6% of the mass is below 400nm and the 94% is above 900nm. The A for Area curves are in between.

If your focus is on volume fractions then the M curve is what you need to know. If you are concerned with yield stress which, according to the YODEL model is proportional to 1/r then because 66% of the radius is in the 300nm range the yield stress will be nearly 3x larger than if you thought that the particles were 1000nm. If you are concerned with the amount of dispersant needed, or are worried about flocculation which depends on radius and surface area, then the A data are important.

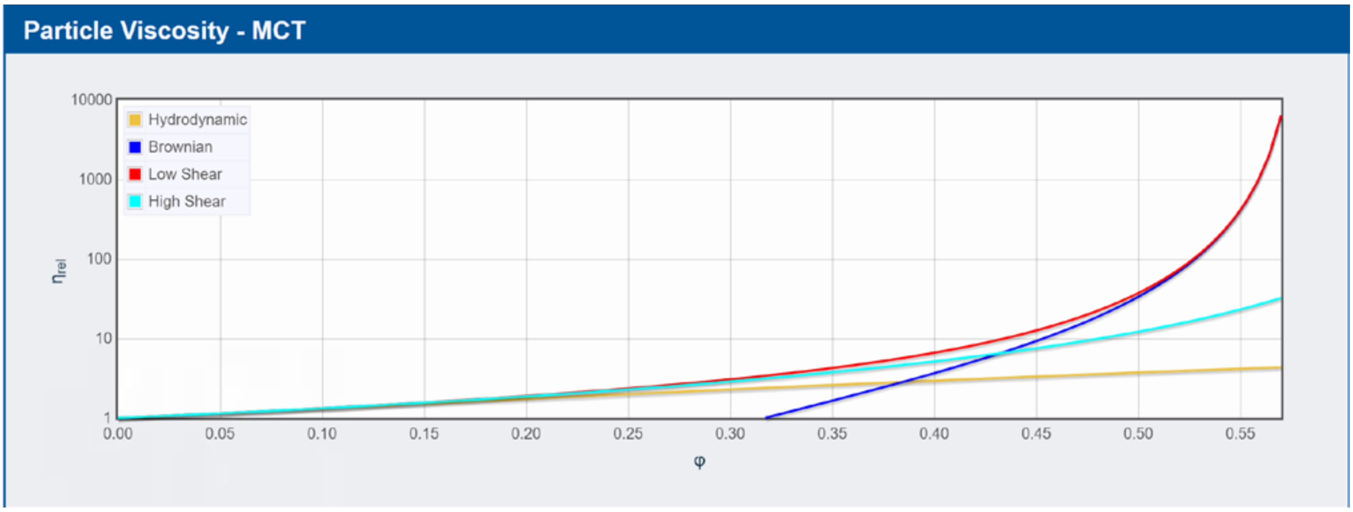
So what is "the" size of these particles. If you take the volume average, ("mean diameter over volume"), this is ... And here we hit a typical problem. We have specified inputs in terms of radius and particle sizes are traditionally measured in terms of diameter. So the volume average, shown as D[4,3] is 1937nm, just below what you would get if you had a pure 1000nm monomodal powder. The number average, D[1,0], is 1082nm, a factor of 1.79 smaller than the volume average. Many users like D50 which is a median based on the cumulative volume distribution - half the particles have a diameter less than this value. If you prefer a different value such as D20 where 20% is smaller than that size you can read it off the graph. The screenshot shows r=969nm so D20 is 1938nm

Many distributions are log normal and the app lets you plot these on a log scale. As mentioned above, a wide log normal distribution allows a higher φ_m value which can help reduce viscosities at high volume fractions.

7.4 Hydrodynamic and Brownian modes

Some of my apps have no user-adjustable parameters, so arguably they should just be presented as graphs. It is generally easier for me to write these as apps and you get to be able to read the values off the graph with your mouse. And if I ever find a way to improve the app by adding adjustable parameters, most of the work has already been done.

The Mode Coupling Theory app is one of these. I like MCT because it provides an insightful partitioning between two types of particulate effects, which helps to build the intuition of what is going on in such systems and how our formulation changes can influence the outcome.



App 7-4 https://www.stevenabbott.co.uk/practical-rheology/Particle-Viscosity-MCT.php

It basically has two calculated curves[29], representing two modes of interaction. The first is the "hydrodynamic" one. This is based on the forces needed to get particles to flow through a liquid. The second is the "Brownian" one, based on the effects of particles bumping into each other. The modes couple to give the third "Low Shear" curve which, not surprisingly, is similar to Dougherty-Krieger.

Because the Brownian mode depends strongly on particle-particle forces the theory here breaks down when the shear is high enough (the High Shear resulting curve) to reduce the Brownian mode or when there are significant flocculating forces in which case the Brownian mode is stronger than shown.

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[29] William B. Russel, Norman J. Wagner, and Jan Mewis, *Divergence in the low shear viscosity for Brownian hard-sphere dispersions: At random close packing or the glass transition?*, J. Rheology 57, 1555-1567, (2013)

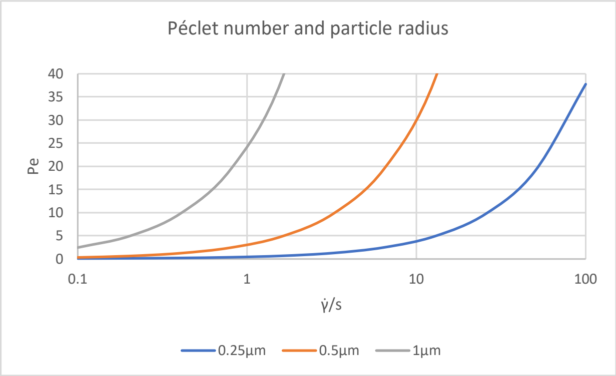
7.4.1 The Péclet number

You often come across the Péclet number, Pe, in discussions of particles and shear rates. This dimensionless number describes the ratio of the movement induced by the flow to the random movement caused by diffusion. It is often considered as a sort of Deborah number. At high numbers >1, the particle motions are dominated by the flow, at low numbers <1 then diffusion dominates. We can express it in terms of $\dot{\gamma}$, radius r and diffusion coefficient D or viscosity (of the background fluid) η:

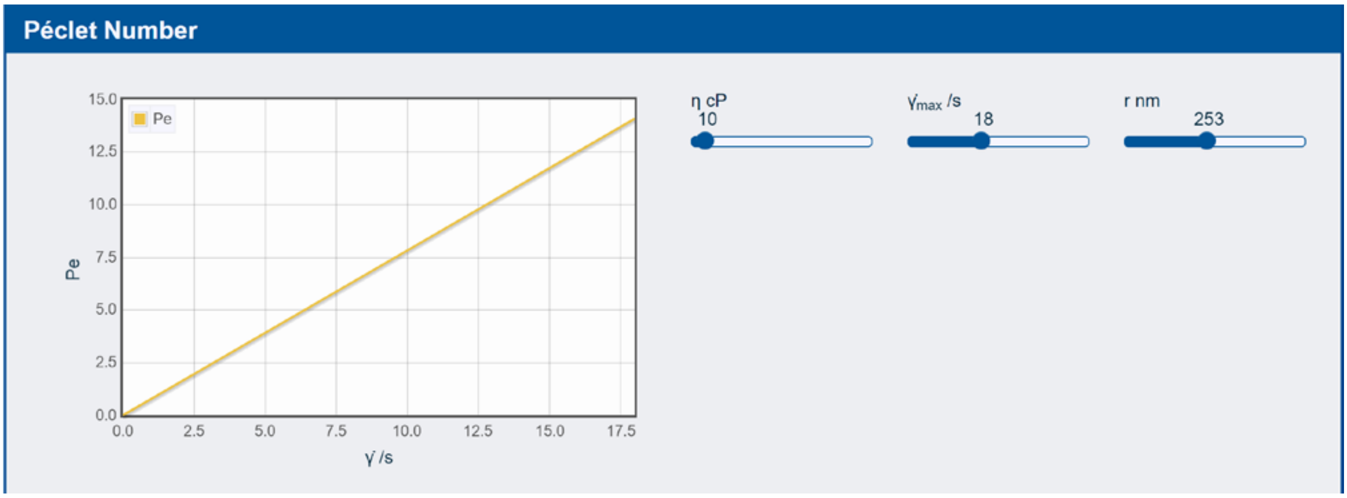
Equ. 7-4

$$Pe = \frac{r^2\dot{\gamma}}{D} = \frac{6\pi\eta r^3\dot{\gamma}}{kT}$$

The idea behind introducing the Péclet number to particle rheology is that a series of plots of viscosity versus shear rate for particles of different radius can sometimes be nicely unified by plotting against Péclet instead of shear rate - i.e. the radius is built in to the x-axis and the radius effects drop out in the plot.



When I first encountered this idea I immediately planned to introduce the Péclet number into various apps. Simplification is attractive when it can be done by such a multiplication. The fact that Péclet does not appear in the apps is because the basic particle viscosity formulae are independent of radius, and cases where Péclet-based plots are helpful in cases of real-world formulae have not been easy to find. This is because although you can do interesting work with small particles at low shear rates which give low Péclet numbers where Brownian effects will be significant, as shown by the graph (the background viscosity is 5cP), for most day-to-day particles above 500nm and shear rates above 1/s, the Péclet number is above 1 so diffusion effects are unimportant. Those who wish to confirm this for their specific system can get the calculations via the Péclet app:



η cP 10

$\dot{\gamma}_{max}$ /s 18

r nm 253

App 7-5 https://www.stevenabbott.co.uk/practical-rheology/Peclet.php

7.5 Shear thickening

When we pour a somewhat viscous cornstarch dispersion into a bath it is a reasonably normal liquid, yet if we try to shear it suddenly by jumping on to it and swiftly walking, it is highly viscous, i.e. it has shear thickened. If we pause to reflect on the mechanism while in mid stride, we sink to the bottom.

The main problem with the classic explanation for shear thickening is that it can be argued both ways (and often is).

The conventional starting point for the explanation is flocculation - the fairly delicate self-association of particles that is explained as being due to a local minimum in the DLVO balance of van der Waals attractions and steric or charge repulsions. Those who have forgotten their DLVO theory can find a handy app at https://www.stevenabbott.co.uk/practical-solubility/dlvo.php. The good thing about flocculating systems is that because the particle-particle attraction is only modest, it is readily broken apart by shear. Shake or stir a flocculated system such as a gel and it reverts to being a normal fluid. So this argues for shear thinning.

To argue the opposite, take a fairly concentrated dispersion and add extra energy via shear. This forces the particles into more intimate contact than they might like, creating a flocculated system with a much higher viscosity. This is the most popular explanation for shear thickening, even though it is at best limited and at worst wrong.

Both effects are entirely reasonable, so why does shear give us either shear thinning or shear thickening?

It turns out that most systems show both types of behaviour, with the shear thinning effect winning in terms of flocculation. The hydroclustering model mentioned earlier, not flocculation, is the most popular explanation for the sudden increase in viscosity in many systems. The model reflects many of the confusing aspects such as the strong effect of particle shape, e.g. where silica spheres are rather immune to shear thickening while fumed silica (irregularly shaped) shear thickens easily.

The basis of hydroclustering is that when particles are close, the fluid flow around them can either send them flying apart (i.e. break up flocs) or start to form "closed loop" flows that correlate the motions of the particles. As this correlation extends to other pairs, long-range order is built up which seriously gets in the way of the fluid flow, giving the high viscosity.

In fact there are multiple mechanisms for shear thickening. The "dilational" mechanism is entirely opaque to me but seems to apply to some systems. It provides a very sudden onset of super-high viscosity and is the sort of thing that might be useful for new types of, say, body armour. And what is supposed to be a classic example, the corn starch, works via a log-jam effect not at all connected to the hydrocluster and dilational mechanisms.

How do you stop shear thickening from happening? The hydroclusters can only form when the particles are close, so their tendency to flocculate is an indication of problems ahead even though flocculation is not the genuine explanation. Typical stabilising dispersants such as polymers attached to the particles can enforce a large-enough distance to counter both flocculation and hydroclustering. Obviously, shear thickening is more likely as you approach $φ_m$ so multimodal systems will be more resistant at a given φ.

If you really want to understand all this then you need a good Stokesian Dynamics program, Apparently it all makes sense if you do. Ever optimistic I wondered if I could create a good-enough Stokesian Dynamics app. It seems that it is way beyond my capabilities and the processing power available to a typical app.

One final word about shear thickening. It seems that a reliable method of implementing an academic flame war is to express a strong opinion on shear thickening. I therefore issue a disclaimer saying that what I have written is some sort of attempt to assimilate what Hoffman, Brown, Wagner and the other greats have said, and that you are entitled to your own opinion about what is really going on.

7.6 Can we apply particle rheology to the real world?

I once had to give a training course on topics that were to be applied to highly-filled particulate formulations. Although I could speak with confidence about many aspects of these systems, their rheology was beyond my then knowledge. So I had to give myself a crash course in particle rheology and out of that came the need to write many more apps and, from that, Practical Rheology. During the training, I was struck by how useful it was to be able to keep going back to the principles contained in the apps, along with the key principles of entanglement and relaxation times to cover the very different timescales in different parts of the processes.

As so often happens in science, once you learn something new, you find it useful in many other situations. Liquid chocolate and liquid cement are very different materials, yet the physics that controls the tricky problems of handling them through production are identical. I just had to learn that "super-plasticizers" in cement perform the same function as lecithin in chocolate (they each reduce the particle-particle E value used in the YODEL model) to be able to apply the physics of cement to the physics of chocolate.

Any models that are simple enough for me to understand and appify are unlikely to be a perfect representation of a complex system. What they do is allow "science-based formulation". Instead of saying "Increasing particle concentration increases viscosity and yield stress" which is both true and rather unhelpful, we can say "Increasing particle concentration over this range of concentrations will tend to have *these* effects and to control them we will need to focus on parameters A, B and C. Because parameters A and B are not, for various reasons, adjustable, that means we must focus on C. So what do we know about C in this case ..."

So the answer to the question in this section is a clear: "Yes".

8 Summary

This is a guide, not a book. It represents what I wish I had known over my formulation career. My hope is that it brings out a few messages about which I am passionate.

- Measuring a few viscosities or even a few G':G" values is not good enough if you want to optimize your formulation efficiently or create imaginative new types of formulations.
- Rheologists do us and themselves a great disservice by choosing to create a bewildering number of plots of the "same" basic measurement. They should be encouraged to plot fewer variants in order to reach a more appreciative audience. And we should use the apps to help translate between confusing plots
- Modern rheometers make it easy to carry out many different measurements - with the downside that we can get swamped by alternatives. So we need to think about the links between key formulation properties and the measurements that can provide insights.
- A lot of polymer-based formulation and associated rheology can best be understood via entanglement. This shows up in different forms in rotational and oscillatory rheology
- Interconversions between (at least) 6 different ways of looking at the same data should become standard for all of us. The interconversion app is one indication that this is both possible and desirable.
- We tend not to think in terms of timescales and the processes that control them. With a few ideas such as Deborah number and WLF and with measured timescales from oscillatory and thixotropic techniques we can better understand how to optimize the conflicting demands of different parts of our real-world processes, especially via relaxation spectra.
- Interconversions should allow us to mix-and-match types of measurements that have their own limitations, allowing us to fill out our understanding of our formulations over a wider range of timescales to better understand performance across a range of real-world processes.
- The trick of providing guesstimates of shear rates and timescales allows us to know from our measurements what our key properties will be under those conditions, or to extend our measurement range in order to determine them.
- Our inability to map between rotational, oscillatory and elongational measurements is deeply unfortunate and a grand challenge to rheologists
- Particle-based formulations can be made more comprehensible via a small set of key parameters.

Because this is an eBook, I will be delighted to update, revise, correct errors, or write new apps. I can only do this with your help. Feel free to email, phone, Tweet or LinkedIn - you can easily find my details on-line.