Toothpaste, Custard and Chocolate: Mathematics gets Messy

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Abstract

This talk will look at mathematical modelling of real, complex fluids in flow situations – some with serious commercial applications, and some just for fun. We'll spend most of the time looking at the chocolate fountain. We'll experience one of the key day-to-day tools of an applied mathematician: scaling analysis; and we'll answer the question: why doesn't the chocolate fall straight down?

Introduction

In this talk I want to give you an introduction to the mathematical modelling of real, complex fluids in flow situations. I'll use the framework of an undergraduate project *The Fluid Dynamics of the Chocolate Fountain* that was done in 2012, but you'll also see snapshots of some of my current research along the way.

The chocolate fountain project is probably the best undergraduate project I've ever offered, both in terms of the attractiveness of the subject and the achievement of the student. In UCL Mathematics, we offer a four-year degree in which final year students undertake a research project, one-to-one with an academic supervisor. It's a great chance for them to find out whether they enjoy research before potentially committing to a PhD project; and it gives them a chance to show what they can really do, beyond the tight timescales of an exam paper. The student on this project, Adam Townsend, started over the summer of 2011 and finished in May 2012, and (uniquely as far as I'm aware in my department) he even did some experiments to go with his theory.

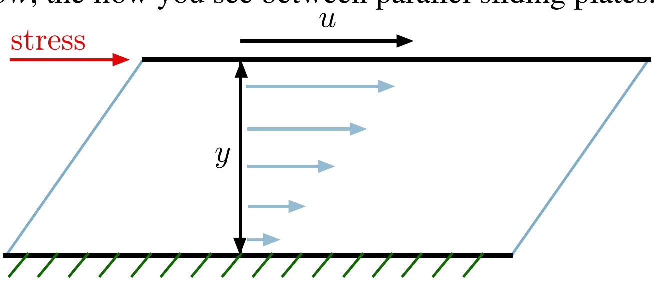
The main topic of this lecture is mathematical modelling. Faced with a chocolate fountain, there are two principal aspects we can model: the chocolate, and the fountain. I'll talk about the chocolate first.

So what is chocolate? We start with a quote:

> Molten chocolate is a complex material – a highly dense suspension of sugar and cocoa solids in a cocoa butter liquid phase – complicated by the variation in composition of cocoa butter with source and harvest. [7]

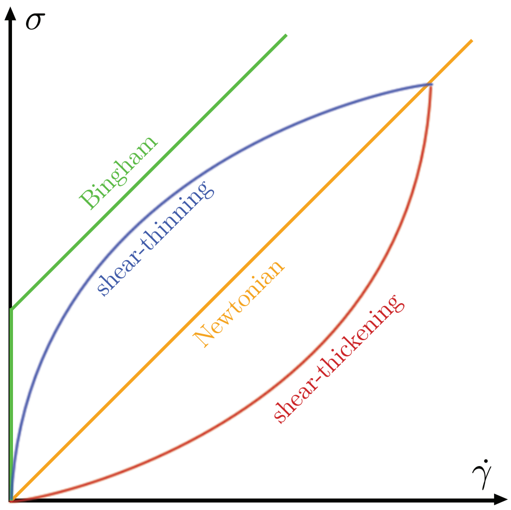
The next question is, how can we model its fluid properties or *rheology*?

We start with an experimental measurement. Ideally, we want all the material in our sample to undergo the same deformation, so that we know we're measuring the response of the whole fluid to that. In practice, there's only one such flow that's not very difficult to set up: *shear flow*, the flow you see between parallel sliding plates.



Dividing the speed of the top plate by the gap between the plates gives us the *shear rate*, $\dot{\gamma}$. We can measure the force (per unit area) required to make the top plate move along; the *shear stress*, σ.

If we then vary the shear rate (use different steady speeds for the top plate), we can generate a graph of shear stress against shear rate:



You'll see that I've given four different categories of curves. Each of these represents a broad class of fluids. Let's have a quick look at each of them.

Straight line through the origin: Newtonian fluid

If the graph is a straight line through the origin, this means that the shear stress is simply a multiple of the shear rate:

$$\sigma = \mu\dot{\gamma}.$$

We call the coefficient μ the *viscosity* of the fluid, and it is a measure of its thickness.

Many simple fluids, containing relatively small molecules – air, water, oil, wine, honey – are Newtonian fluids. There is a huge amount of research into their dynamics, which governs the oceans and atmospheres and much else besides. But I'm more interested in the other curves: so-called *non-Newtonian fluids*.

Graph curving upwards: shear-thickening fluid

We can still define the steady shear viscosity at any point on our curve, just by rearranging the equation we had for the Newtonian fluid: $\mu = \sigma/\dot{\gamma}$. But now we find that the viscosity μ increases as we increase the shear-rate $\dot{\gamma}$. This means the fluid gets thicker, more solid-like, the faster we drive it.

This is fairly strange behaviour, and only a few materials do it: a cornflour-and-water mixture is one of the most dramatic examples. If you search online for *oobleck* you'll find many excellent videos of people running on this (and then standing still and sinking). Researchers have been trying to get to the bottom of this extreme version of shear thickening (known as discontinuous shear thickening) for decades, and have recently started to approach a theoretical understanding of the microscopic forces at work.

We try to understand this by creating mathematical models of the physical system, containing only specific simple pieces of the complexity of real suspensions. Over many years, a consensus has built up that discontinuous shear thickening needs any model to include some frictional forces which only happen when particles are squeezed together very strongly. Then increasing the flow speed can increase the number of particle pairs which feel these extra, frictional forces and effectively make the suspension feel as if it has more solids in – bringing on jamming. These are essential ingredients; but my group's work [6] has shown that small amounts of friction (of the sort you'd get between a book and a table, for example) are not enough to cause the jamming: you need forces of a much larger magnitude. And research is continuing…

Whether we understand it or not, the phenomenon is hugely useful: Norm Wagner and colleagues at the University of Delaware [3] have discovered that Kevlar impregnated with one of these fluids is much more effective than normal Kevlar at stopping bullets!

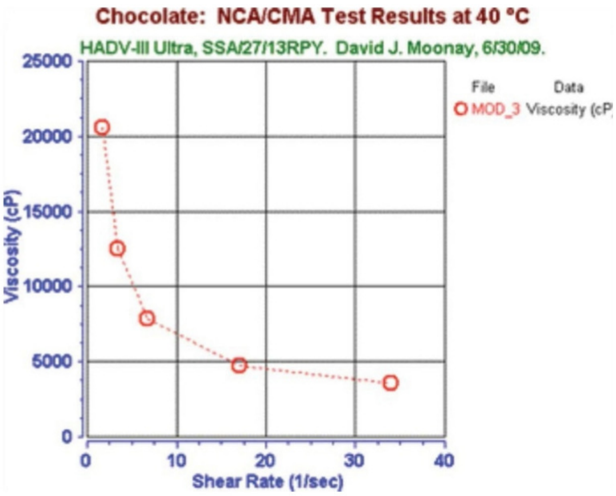
Line that stops above the origin: Bingham fluid

The key feature of this class of materials is that the graph of shear stress against shear rate doesn't appear to go through the origin. It does, of course: for any material, if you don't apply any force to the top plate it won't move. But the converse isn't true for these materials: you can apply a small force to the plate and the material inside will resist like a solid. It might move a short distance, but it won't flow and keep flowing. This is called a *yield stress*: there is some structure holding the material together that takes a finite stress to break it down and start flow. Typical examples include whipped cream, tomato ketchup, and toothpaste.

Toothpaste needs to have a yield stress for purely aesthetic reasons: we, as consumers, like our toothpaste to sit up nicely on the brush before we put it in our mouths. I'm working with a group of engineers and a toothpaste manufacturer to understand exactly where the yield stress comes from: it's one of the least reliable parts of the manufacturing process, and there's a real risk of making a huge batch of toothpaste that tastes right, has the right chemical composition, does the job but *can't be sold* because it won't look right on the brush! The paste is a complex mixture of different-shaped solid particles (smooth ones to make it thicker, jagged ones to clean your teeth) and a surrounding fluid which is itself very complex, so this is challenging research!

Line that curves downward: shear thinning fluid

The last class of curves is those that curves downwards. This means the viscosity *decreases* when the flow rate increases, and these fluids are called *shear-thinning fluids*. This usually happens because some microscopic structure either breaks down, or aligns, under fast flow, making the system as a whole easier to deform. Many examples are designed to exhibit this behaviour: paint, for instance. When you carry your loaded paintbrush from the tin to the wall (very low flow rates), the paint needs to be fairly thick so it will not drip off. But when you're brushing it onto the wall (high shear rates) you need it thinner so it will spread without huge amounts of effort. And finally, once you stop brushing (back to low shear rates) you need it to thicken up again so that it doesn't have time to run down the wall before it dries. Other examples of shear thinning fluids include nail varnish (again, by design), lava and – as it turns out – molten chocolate, as we can see below.



Graph of viscosity against shear rate for dark chocolate at 40 degrees C. Taken from [2].

Modelling chocolate

Before we can do any mathematical calculations about the flow involved in a chocolate fountain (or any other chocolate flow), we need to capture the behaviour of the material with a governing equation. The *constitutive equation* is a relation which determines the stress in a complex fluid from the flow conditions, the temperature, and the whole flow history. Some materials carry a lot of information with them – for example, in a polymer melt (e.g. molten plastic, on its way to becoming a moulded product) the molecules can become aligned by the flow and there is a component of the stress that relates to their "desire" (actually driven by entropy) to relax back to a non-aligned state [4]. In fact molten chocolate also does this to some extent [1], but it's a fairly weak effect so we won't take it into account here.

We choose to use a *generalised Newtonian fluid* model to describe the behaviour of chocolate. That means we assume that the only complicated thing going on is the dependence of the viscosity on the deformation rate (shear rate). All that remains is to choose the form of the function $\eta(\dot{\gamma})$ defining it. There are three standard models we can look at.

Newtonian fluid This is the simplest possible model, in which the viscosity does not depend on the shear rate at all

$$\eta = \mu$$

It's not a particularly good model for chocolate, but there are several reasons for doing it anyway. First, it's easier than any of the others, so you can try out calculations before getting bogged down in the difficult calculations. Second, lots of fluids are Newtonian, so many of these calculations have already been done in the literature. And finally, it's a special case of many of the models that fit better, so it gives us a limit case to check correctness when we do a more difficult calculation.

Power-law model This is typically the first model anyone uses when they want to incorporate non-Newtonian effects without introducing too many new unknown physical parameters into the model. The amount of shear-thinning is captured by a single new parameter, the flow index n:

$$\eta = k\dot{\gamma}^{n-1}.$$

Now we have two parameters, the viscosity scale k and the flow index n. In the case $n = 1$ and $k = \mu$ we recover the Newtonian model above.

You might wonder why we're using $n - 1$ as the power. The reason is that the physical quantity we can measure directly in experiments is not the viscosity itself, but the shear stress

$$\sigma = \eta\dot{\gamma} \qquad \sigma = k\dot{\gamma}^n.$$

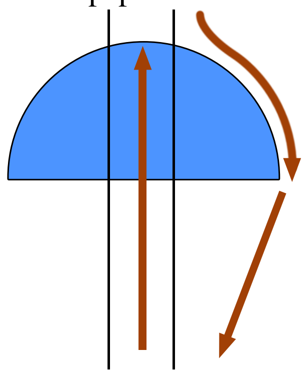
Casson's model This more complicated model shows both shear-thinning and a yield stress, and can only simply be expressed in terms of the shear stress:

$$\begin{aligned} \sigma &= \left(\sqrt{\mu_c \dot{\gamma}} + \sqrt{\sigma_y}\right)^2 && \text{if } \sigma \geq \sigma_c, \\ \dot{\gamma} &= 0 && \text{if } \sigma < \sigma_c. \end{aligned}$$

It was the official standard of the International Confectionery Association from 1973–2000, at which point it was observed that it was difficult to use because of the yield stress, but also inaccurate at low flow rates (where the yield stress is relevant). They now recommend ad hoc empirical modelling, which in practice usually means a collection of power-law models for different applications. From here on we will only use the Newtonian and power law models.

Modelling the Fountain

We chose to split the fountain into three regions, with quite different flow dynamics in each. Each one has its own story to tell. There isn't space here for a full discussion of all of them, but I will briefly summarise what we discovered. The full details have been published [5] in an academic research paper that is freely available on the web.



Central pipe flow The reality of the pumping flow up the central core (at least in the fountain we bought) is a screw pump, which induces a complex, fully three-dimensional rotating flow pattern. We observed that the rotation was almost completely dissipated before the chocolate came pouring out at the top (and made the practical decision that an undergraduate project didn't have time for 3D computer-based simulations) and discarded physical reality for this part of the flow. Instead we worked out the flow profile for a purely pressure-driven flow through a pipe. This was an excellent way to get used to using the non-Newtonian fluid model. Once we made some sensible assumptions about the flow being steady and in the direction we would expect, the equations became completely manageable. The flow is always fastest in the centre of the pipe, and static on the walls; a shear-thinning model leads to small layers close to the wall where most of the shearing happens, and where the fluid becomes thinner; and a central plug-like region of thick fluid being transported by the thin lubricating layer.

Dome flow This time when we started from the governing equations, and made all the same sensible assumptions we'd made last time, we were still left with three coupled partial differential equations to solve, only one of which was simple. So we had to use some physical approximations to make progress.

We observed that the thickness of the layer of chocolate on the dome was much less than the distance it travelled, which was of the same order as the radius of the dome itself. Then, because of *mass conservation* – our experiment can't create or destroy chocolate, only move it from place to place – we can argue that the velocity parallel to the dome surface must be much larger than any velocity perpendicular to the surface. This is a *scaling argument*: we argue that some terms have to be much smaller than others in our equations, and then discard the small ones to get a slightly inaccurate mathematical formulation that we can solve, and whose solution is close to what happens in reality.

By the time we'd finished our scaling analysis, the only physics left in our equations was a balance between gravity pulling the chocolate down the dome, and viscous forces slowing it down. This same balance appears in all sorts of *thin film flows*, including painting, the flow of lava down a volcano, and even the dynamics of the thin film of tears in your eye.

The end conclusions looked surprisingly similar to what we found in the pipe flow: increasing the shear-thinning caused a thin lubrication layer close to the dome, with a layer of more viscous chocolate flowing on top of it.

Falling curtain The falling curtain of molten chocolate is the whole point of the chocolate fountain. It's where you dip, after all. It's also surprisingly difficult, both practically and mathematically. Practically, we found that the sheet is subject to instabilities, especially as the chocolate starts to run out and the volume coming out of the top of the fountain reduces. There is a tendency for the curtain to separate into a series of vertical streams, which move around, sometimes reaching the pool of chocolate at the base and sometimes dripping and rebounding upwards. This was well beyond the scope of what we could model at the time (though people have had a go since, including Lyes Kahouadji in Omar Matar's group at Imperial College).

Mathematically, even if you assume a smooth, steady flow, it's still difficult because there are two free surfaces – when you start, you don't know the thickness of the sheet or the trajectory of its centreline. You don't even know how it leaves the dome (that thorny issue, known as the *teapot effect*, turns out to involve some surface chemistry which is well beyond me). The best we could do, in the end, was to take someone else's computed solution to a similar problem and scale it to fit our situation. The key conclusion: the most important force acting is surface tension, which is the reason the curtain falls inwards and not straight down.

Conclusion

This lecture has skimmed the surface of rheology, which is a huge interdisciplinary research area spanning mathematics, physics, chemistry and engineering. On the chocolate fountain itself, we've seen in the central pipe flow that shear-thinning fluids tend to form a plug-like central flow; on the dome we've discovered the joys of scaling analysis and found that the main things that matter are gravity and viscosity; and in the falling curtain flow we've seen that it's surface tension pulling the sheet inwards.

Looking at non-Newtonian fluids more broadly, we've seen that chocolate fits, with paints and lava, into the class of *shear-thinning* materials; but we've also seen some other classes of material. Materials with a yield stress can resist a certain amount of force before they flow; and shear-thickening materials like cornflour can even be used to stop bullets.

I hope I've whetted your appetite in more ways than one!

References

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