

# The Non-Newtonian Thermal Properties of Heinz Tomato Ketchup

Author: D. J. Fulton.

Experimentalists: D. J. Fulton and Jade Watt.

Date of the experiment: February 2015. Date of the report: 22nd April 2015.

In this paper we examine the temperature dependence of the empirically determined parameters used in the Armand de Waele Relation, the power for fluids. We find a strong pattern emerges within the data, one that we cannot explain using any simple model. We also look at the theory of the shear thinning that the power law describes and its relation to thixotropy. We propose and carry out an experiment based on the theory of thixotropy to relate this concept to measureable properties of the fluid. We find that increasing temperature dampens the rate of thixotropic decay and appears to reduce the degree of entanglement within Ketchup, which acts as a physical gel.

## Introduction

The properties of non-Newtonian fluids are of great importance. Over the last several decades technology based on these complex fluids has flourished and is in use both in industry and home personal use. Thus our ability to understand and predict how these substances behave is of great utility.

In these works, we examine the non-Newtonian properties of *Heinz Tomato Ketchup* as a particular example of a pseudoplastic and thixotropic fluid in order to gain some understanding of these principles. We will also examine how these two properties relate to each other and how they vary with temperature.

A pseudoplastic [1] is a fluid that exhibits shear thinning. This is a useful property purposely engineered into household and industrial paints and often used in pharmaceuticals. One common model used to describe shear thinning properties is the Armand de Waele Relation also known as the power law of fluids [1]. It is very widely used and has the benefit of being very simple. The equation is as follows.

$$\mu_{eff} = K\dot{\gamma}^{n-1}, \quad (1)$$

where  $\mu_{eff}$  is the effective viscosity,  $K$  is the flow consistency index,  $\dot{\gamma}$  is the shear rate and  $n$  is the flow behaviour index. This equation is empirically derived and the parameters  $K$  and  $n$  may only be found experimentally.

A thixotropic fluid [2] is one that exhibits a time dependent viscosity and is often an unwanted effect of engineering shear thinning properties into a substance. As a fluid with these properties is sheared at a constant rate the viscosity decreases, tending asymptotically towards a minimum value. Corollary to this effect is that when a thixotropic fluid is sheared at a high rate and suddenly returned to shear at a lower rate the viscosity will increase, tending asymptotically towards a maximum value. These two effects we will refer as the 'decay regime' and the 'recovery regime' respectively. The models we will be employing to describe these behaviours are two forms of the unstretched exponential model [2]. They are as follows, where Eq(2) is used to model the decay and Eq(3) to model the recovery.

$$\mu_{eff} = \mu_{MIN} + \Delta\mu_D \cdot \exp\left(-\frac{t}{\tau_D}\right). \quad (2)$$

$$\mu_{eff} = \mu_{MAX} - \Delta\mu_R \cdot \exp\left(-\frac{t}{\tau_R}\right). \quad (3)$$

In these two equations  $\mu_{MAX}$  and  $\mu_{MIN}$  are the maximum and minimum effective viscosities after shearing for an infinite time and resting for an infinite time post-shearing respectively;  $t$  is the time since the start of measurement;  $\Delta\mu_R$  and  $\Delta\mu_D$  are the differences between the start viscosity and  $\mu_{MAX}$  and  $\mu_{MIN}$  respectively and  $\tau_R$  and  $\tau_D$  are the recovery and decay constants respectively.

## Theory

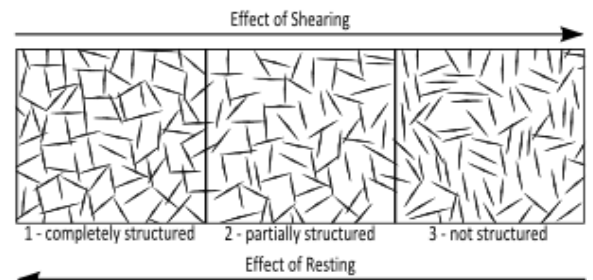


fig.1 - Showing the variation of internal structure of a fluid consisting of many long chain polymers.

Pseudoplasticity and thixotropy can be explained by considering the internal structure of the fluid. Ketchup in particular, due to its abundance of long chain sugars, proteins and fibre, acts as a physical gel. It is the entanglement of these long chain molecules that give ketchup its viscosity and is responsible for the non-Newtonian properties it shows [3]. Fig.1 above shows a simplified diagram of how the internal structure varies. It is easy to intuit that the unstructured fluid will flow more readily than the structured sort and so have a lower viscosity.

As Ketchup is sheared, starting from rest, its physical bonds are broken by this agitation where the rate of breakdown, is dependent on the shear rate and the amount of bonds left unbroken. This is counteracted by the rate of formation of these bonds caused by their tendency to entangle under Brownian motion. This is a function of temperature and the amount of bonds

unformed. An equilibrium is reached when these effects are balanced.

Shear thinning is a product of this balance, as the shear rate at constant temperature sets the equilibrium structure for the fluid. However, this value is not reached instantaneously and this is what causes the thixotropic, time dependent, properties. In some pseudoplastics the rate of breakdown and recovery of these bonds is so rapid that the thixotropic properties go unnoticed, but all shear thinning fluids exhibit this property to some extent.

Our hypothesis, and one of the focuses of this study, is that the recovery of the viscosity of ketchup post-shearing will show a strong relation to temperature. Particularly we expect that  $\tau_D$ , the recovery constant, will decrease with temperature representing the recovery being completed in a shorter period. We expect that at higher temperatures the increase in Brownian motion will cause a greater rate of entanglement. We arrive at this by assuming that the only thing needed for entanglement is that the molecule chains be particularly arranged as to be interlocked and that once they reach an entangled state they become fixed in position. The arrangement has no relation to temperature, only to position. Therefore the rate of recovery is only dependent on the rate of sampling these positions. This will increase with higher temperature and cause a faster recovery.

Supplementary to this we wish to probe how the thixotropic decay and power law model parameters are affected by changes in temperature. We will search for any patterns that may emerge in how these models' parameters vary with temperatures that might themselves be understood and modelled.

## Methods

To collect our data we used a Brookfield DV2T Viscometer which was calibrated to the manufacturers standards [4]. To reach and maintain our desired range of temperatures we used the Brookfield TC-650SD Water Bath which was connected to a water jacket around the vial containing the sample [5].

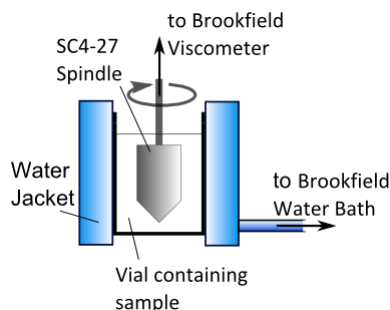


Fig.2 - The experimental set up.

Chronologically, our first period of tests was to find how the power law parameters changed with temperature. Between 10 and 65°C at 5°C intervals we measured the viscosity at a range of shear rates between 0.034 and

21.110 s<sup>-1</sup>. In order to allow for the thixotropic nature of the ketchup, at the start of the test we first sheared the fluid at its lowest test speed of 0.034 s<sup>-1</sup> for 15 seconds so that the value we measured at the end of this period would be closer to the equilibrium viscosity for this shear rate. Then for the subsequent measurements we moved up our shear rate range periodically, leaving 10 seconds between changing the speed and recording the viscosity. We used the same ketchup sample throughout each session due to time constraints. However in order keep the shear history similar for all our sets of data we took precautions to first run the full test once through at the start of the session and discard that set of data before running it again to collect results. This should simulate a shear history in our ketchup sample that would be similar to the shear history in subsequent tests so as to keep it as constant as practically possible. We also kept the time between tests a constant at 5 minutes to allow some recovery of the fluid and to allow time for temperature changes if required. We repeated each test 3 times and then moved one step up our temperature range. We note that we did not have a practical method of measuring the temperature of the sample directly. Thus we had to make the assumption that after 5 minutes for the heat to dissipate through the sample it would have reached the new temperature of the water bath. This temperature step was kept at only 5°C.

Following our experiment we fit our averaged data to the power law Eq.(1) and using a method of least square fitting found the model parameters for each temperature.

Our second period of tests was on the thixotropic nature of ketchup. At temperatures between 10 and 80°C we took measurements of the viscosity at 1 second intervals at a constant shear, first in the decay regime and then in the recovery regime.

For our experiment we choose 15.300 s<sup>-1</sup> as the higher shear rate used for the decay test and for the pre-shear for the recovery test and chose 0.170 s<sup>-1</sup> as the lower value for the recovery test. We ran these experiments sequentially, first completing the decay test and then immediately after, the recovery test.

We recorded the decay regime for the first 61 seconds from introducing our shear and the recovery regime for the first 301 seconds following our drop in shear rate. We then fit our model to this data as described previously.

## Results

The relationship between temperature and the power law modelling parameters are shown below in fig.3. We noted in the process of fitting that our data did not adhere to the power law model well at lower shear rates and when calculating the value of Chi-squared,  $\chi^2$ , we noticed that lower shear rates were the main contributors to this value. This poor fit is a criticism often made against the power law and one of its drawbacks. We therefore opted to only consider the data above the shear rate of 2.6 s<sup>-1</sup> when determining the best model parameters.

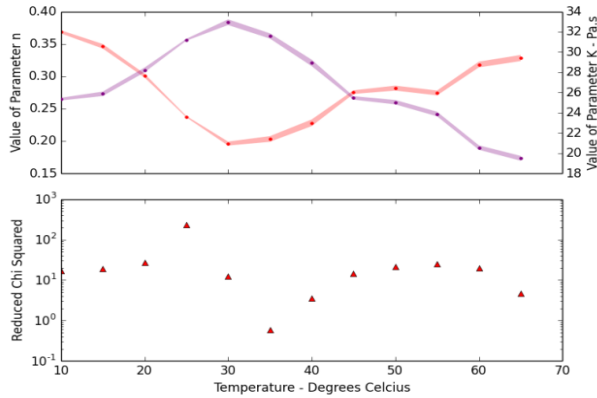


fig.3 - Showing the power law parameters across a range of temperatures. Values  $n$  and  $K$  are shown in red and purple respectively in the top plot and plotted with their error region (see appendix). The reduced Chi squared value of each individual fit is shown in the lower plot.

We also noted a pattern in our residuals of each individual fit to the power law. Fig.4 shows the fit and residuals of shear thinning at 20°C as an example. We saw similar residuals across all the power law data and when viewed as a percentage error of the value these residuals appeared to have a sinusoidal form.

In the figures for the rest of this report the top plot will show the raw data as red markers along with their shaded error region (see appendix) and the model fitted as a black line. The lower plot will show the residuals to the fit as red markers with their shaded error region.

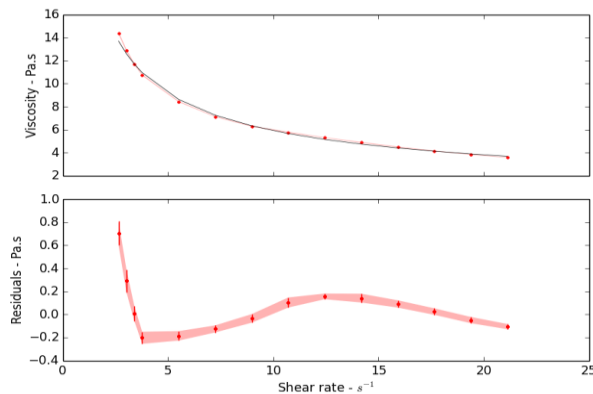


fig.4 (above) - Shear thinning at 20°C. Reduced  $\chi^2_{min}$  of 26.9.

From our thixotropy experimental epoch, here we show the recovery and decay curves of ketchup at 20°C in fig.5 and fig.6 respectively.

These figures are typical of the results that agreed with theory and show the fluid recovering and decaying at a exponential rates, however we could not repeat these same observations at all temperatures.

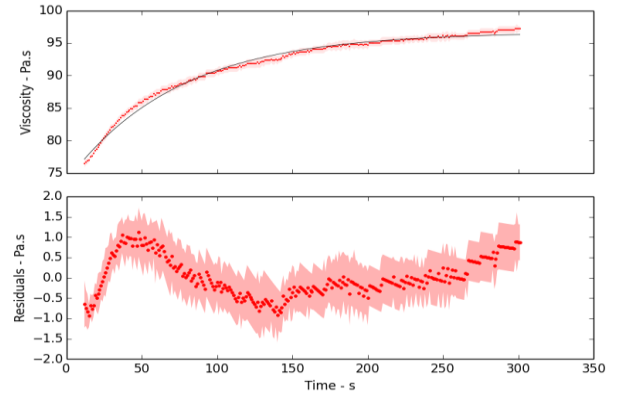


fig.5 (above) - the recovery regime of Ketchup at 20°C. Reduced  $\chi^2_{min}$  of 1.17.

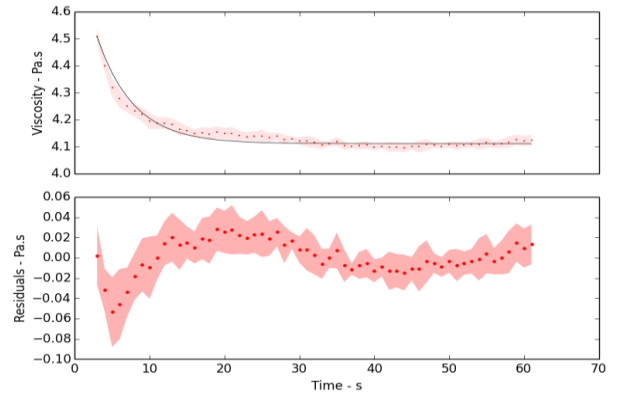


fig.6 (above) - The decay regime of ketchup at 20°C. Reduced  $\chi^2_{min}$  of 0.85.

We achieved similar recovery patterns for temperatures of 10 and 60°C. At 30°C our model broke down and the recovery pattern became linear and furthermore at 40, 50, 70 and 80°C it broke down altogether and the viscosity actually decreased or varied sinusoidally with time.

In the decay regime we achieved similar results and residual patterns to fig.6 at temperatures in the range 10-70°C but conversely at 75 and 80°C the viscosity increased with time. However when  $\mu_{MIN}$  and  $\tau_D$  from the decay regime were plotted against temperature we saw weak downward and upward trends respectively for the data of 10-70°C. However as they were only weak trends they have not been plotted here.

Below, as an example we have shown the residuals of the recovery regime data for Ketchup at 70°C. The data itself showed no overall recovery or decay, the fit was a constant line but the residuals were of interest. As you may note, this has a very strong periodically repeating pattern. This same pattern was obvious in all of our recovery regime data and always had the same frequency of  $8.35 \pm 0.19$  mHz.

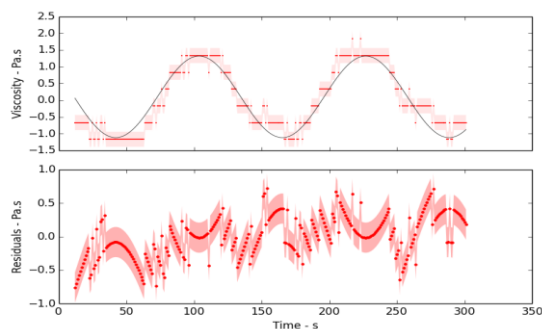


fig.7 - the modelled residuals of the recovery pattern at 70°C. The top plot shows the modelled residuals to a constant value fit and the lower plot shows the residuals to this. Reduced  $\chi^2_{min}$  of 1.33.

## Discussion

Firstly we would like to tackle the issue of the periodicity observed in the recovery regime as it may have implications to the rest of our data. The reader will note that there is clearly a very strong periodicity in this data set which is approximately sinusoidal. The frequency of this perturbation is concurrent with the angular frequency of the spindle for this test. The spindle having frequency of 8.33 mHz. This leads us to believe that our viscometer during this experimental period was at fault. We also noticed by inspection during the experimental that there was a slight misalignment of the spindle with the rotor axel. We could not correct this fault ourselves during the experiment. We therefore suspect our work here to have systematic error within it caused by this. Based on the clear manifestation of this error in the recovery data we expect that it may also be the cause of the patterns observed in many of our other residuals, which also had a sinusoidal form when expressed as a percentage of the value. This perturbation was also the reason that we could not extract much meaningful data from the recovery regime as there was too much noise.

Despite this annoyance, the results of our evaluation of the power law parameters we achieved were quite interesting. We measured all values to a high precision but it must be noted that the large Chi values mean that it is somewhat inconclusive as they were mostly poor fits, with an average minimum reduced Chi squared value of approximately 15. Although, we suspect that the high Chi values may have been due to our handicapped viscometer and that the power law would in fact be a good description of the fluid in the absence of this effect. In spite of this the results show a simultaneous minimum  $n$  value and maximum  $K$  value at 30°C. Physically, this means that the fluid at this temperature has its greatest shear rate sensitivity and maximum viscosity range.

Evaluation of the results of our thixotropy experiments show considerable success in fitting an inverse exponential to the decay regime, we note that it was only at high temperatures that the model broke down and this most likely was due to chemical changes in the ketchup as it was essentially cooked at 75 and 80°C. The pattern we observed in the decay parameters below 75°C

indicate that the fluid was taking longer to decay but reaching a lower minimum viscosity with increasing temperature. This implies that the effect of temperature is as a source of damping on the decay and that with increasing temperature the equilibrium reached shifts towards being more unstructured. The trend in the minimum viscosity suggests that there is an extra effect that we didn't take into account in our predictions of the recovery, that less bonds are formed, less entanglement, with increasing temperature. The same general decrease of viscosity with temperature can be seen on comparison of the shear thinning curves, the higher temperature curves showed generally a lower viscosity than the cooler ones. This may be because the vigour of the thermal motion at higher temperatures is enough to break some of the bonds that would have been formed at lower temperatures, resulting in a lower degree of structure. In the recovery regime, we would expect this to manifest in  $\mu_{MAX}$  decreasing with temperature but still expect the recovery constant to decrease with temperature. However we were unable to test these new hypotheses concerning the recovery regime. We had some success fitting the unstretched exponential model but were greatly vexed by our broken viscometer. So although our model fits partially in this regime we don't have complete enough data say how the parameters vary.

## Conclusion

In conclusion, we have found a curious thermal dependency of the power law parameters of *Heinz Tomato Ketchup* which reaches its peak shear thinning capacity at 30°C. We also note the thixotropic decay and recovery of ketchup can be modelled with some success as an exponential but we were severely vexed in this enterprise by a fault in our equipment. We noticed that with increasing temperature the time for the thixotropic decay to reach equilibrium increased and the minimum viscosity after shearing for an infinite time decreased. This indicates the internal structure of the fluid decreases with temperature, as we would expect, and that the increase in thermal motion from increased temperature disrupts the macroscopic breakdown of the internal physical bonds.

## References

- [1] Rheology School, *The Power Law*, [http://www.brookfieldengineering.com/education/rheology\\_papers\\_benchmark\\_products.asp](http://www.brookfieldengineering.com/education/rheology_papers_benchmark_products.asp), accessed April 2015
- [2] J. Non-Newtonian Fluid Mech., 70 (1997) 1-33, *Thixotropy, A Review*, Howard A. Barnes, Unilever Research Laboratory, Bebington.
- [3] *Soft Condensed Matter*, Richard A. L. Jones (OUP 2002), Chpt. 2, Oxford University Press.
- [4] BROOKFIELD DV2T, Viscometer Operating Instructions, Manual No. M13-167-B0614, pg8.
- [5] BROOKFIELD TC-650 Operators Manual, Circulating bath with Digital Controller, section 1.4.

## Error Appendix

### The Error Region

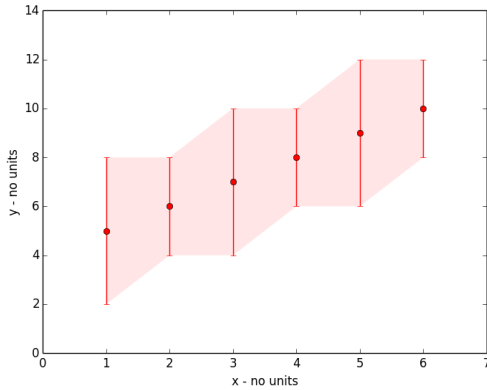


fig.8 - A demonstration of the error region used in this paper.  
The area shaded in pink is the defined region.

The 'error region' as referred to throughout this report is defined as the region enclosed by drawing straight lines adjoining the maximum limit of standard error bars and the minimum limit of these error bars. In fig.8 the pink shaded area contained within the standard error bar extremities is the what we define as the error region. Although unconventional we chose to show our error in this manner as it is an advantage when the errors are so small as to be obscured by the data points or when there is so much continuous data that with standard error bars the plot becomes too crowded. We found both these cases applied within our works.

### The Equipment

The Brookfield DV2T Viscometer has a standard accuracy of  $\pm 1\%$  of the full scale range. We adopted to use the SC4-27 spindle and to operate in the RV torque range, this reads to values of 0.55Pa.s and explains both the obviously discrete data and the error bars shown in fig.7. The data is discrete to 0.55Pa.s and the error bars assumed were half this division.

The Brookfield TC-650SD Water Bath has a temperature stability of  $\pm 0.04^\circ\text{C}$ . However the main error in temperature would be due to the dispersion of heat throughout the fluid. This is hard for us to practically measure or estimate given our equipment so we have ignored these potential errors in our analysis.

### Errors in the Modelled Data

To calculate the errors of the power law measurements we repeated the test three times and took the standard error of each individual data point. We chose to do it this way as it was the chaotic nature of the fluid that was the limiting factor to the accuracy of our measurements and not the limits of our equipment.

For the thixotropic experiments we calculated errors on the data using the same approach as we did for the power law data. However, due to time constraints we could not repeat all our measurements three times, therefore the tests at 10, 30, 50, 75 and  $80^\circ\text{C}$  we assumed to have the same errors as the data at  $20^\circ\text{C}$ .

The error in the power law parameters  $n$  and  $K$  were calculated by  $\chi^2_{\min} + 1$  targeting [a].

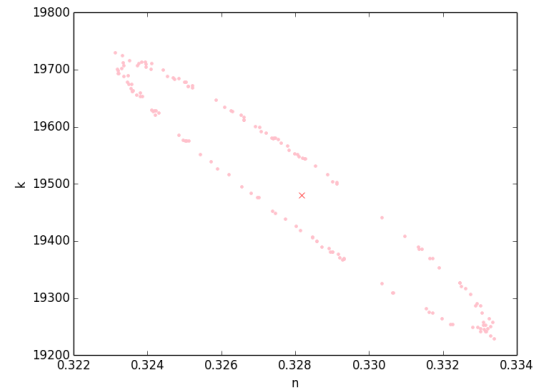


fig.9 - The error surface of the power law fit to ketchup at  $65^\circ\text{C}$ .

This was achieved using a computer modelled gradient decent method which generated a series of co-ordinates accurate within 0.05 of the  $\chi^2_{\min} + 1$  value, as shown above. We took the maximum and minimum extents of this region as the maximum and minimum extents of the uncertainty in our data.

### General Discussion

The errors discussed here are in the ideal case, they are most likely an underestimate. The power law parameters are given to pseudo-precision as we calculated very low errors, typically 1% but these are most likely not correct due to the poor fit of the models, hence our high  $\chi^2_{\min}$  values.

It is also hard for us to estimate the effect that our substandard viscometer had on our data, although we can assume that the accuracy was less than the value quoted by the manufacturer. We were unable to take this into account.

### Appendix References

[a] *Measurements and their Uncertainties*, Hughes & Hase, Oxford University Press.