THE MEASUREMENT OF SURFACE TENSION AT HIGH TEMPERATURES ON GLASS SAMPLES USING THE DROP PROFILE ANALYSIS

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Premise

The measurement of the surface tension on glass at high temperatures is always troublesome, because of the inherent difficulties of the measurement. Surface tension can not be measured directly but it needs to be computed mathematically from the measurement of other physical properties.

Methods like the torsion scale with the platinum ring, or the weight of a drop, which are widely used to measure surface tension on liquids at room temperature, are quite difficult to apply on molten glass. In the glass industry the measurement of surface tension is commonly carried out using the method of the pendant wire, heated with a platinum loop. This method is quite simple and inexpensive, but it suffers of a poor temperature control, beside the fact that it is impossible to carry out the test over a wide range of temperatures.

In the last 20 years a new method for the measurement of surface tension gained more and more credit, even though it was conceived more than 200 years ago. The two genius of mathematics Laplace and Young wrote the equation which describes the shape of the separation surface between two fluids as a function of the density of the two fluids and of the interfacial tension. This equation, known as Young-Laplace, can be used to compute the surface tension of a drop of liquid, knowing the density at the temperature of the measurement and analysing the shape of the drop.

Now a day there are several instruments available on the market which perform the measurement of the surface tension based on this principle, but all of them work only up to few hundreds degrees.

The new drop analysis

Expert System Solutions has recently implemented the measurement of surface tension based on the drop shape analysis using the Young-Lapalce equation on his heating microscope MISURA 3. This new release make it possible to get reliable measurements of surface tension up to 1600 °C.

Fig 1: The heating microscope MISURA 3 by Expert System Solutions

In order to achieve this result, a new algorithm was developed, based on the following mathematical assumptions.

Inside of a drop of liquid, the pressure on the concave surface from the inside is higher than the pressure on the outside convex surface, and the difference of the two pressures depends on the interfacial tension and on the radius of curvature of the surface. For a drop laying on a surface (sessile drop), the surface is not spherical but it has axial symmetry and in each point the curvature can be described using two radius of curvature on normal planes.
The Young-Laplace equation is then in the form:

$$p_1 - p_2 = \gamma \cdot \left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

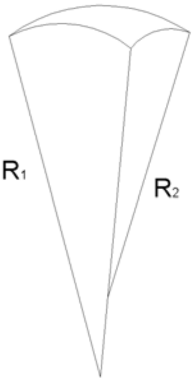

Fig.2 For a sessile drop there are two different curvature radius for each point of the surface.

The first attempts were made many years ago, using this equation to derive the value of γ from pictures taken with a camera using a simple conversion table which expresses γ as a function of the maximum drop diameter and the diameter at the height h equal to that diameter. This method, known as "Fordham table" gave inaccurate results, because the drop profile was measured only in one point. As a final result, the method of measurement of surface tension from drop profile gained a bad reputation.

Recently, thanks to the extreme computational speed of the new generation of processors it is possible to exactly compute the complete profile of the drop solving the Young Laplace equation for all the point of the profile.The equations needed to solve the problem were developed step by step by several scientists, in the whole time lap of the last two centuries.
The method that we applied is based on the Bashforth-Adams differential equation, which, unfortunately, has no known analytical solution.
The solution is found applying the Runge-Kutta numerical integration and then minimising the mean square deviation between the calculated and the actual drop profile until the error falls below 10 $^{-4}$.

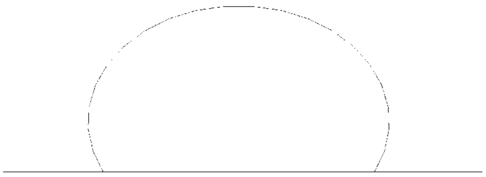

Fig 3: computed drop profile

The problem of the density

After solving the math, there is another problem to approach: now we can solve the equation for each point of the profile of the drop, but the differential pressure on the two surfaces of each point of the drop is dependent on the density of the two fluids.
The fluid surrounding the drop is air, and the density of air at any given temperature can be found in literature. We use a function which interpolates actual measurement from 100 K to 1600 K with a mean square deviation of 3 x 10^{-5}, and we are searching no further.

The problem is to know the density of the molten glass at the temperature of each measurement. At a first approach this looks, again, like a problem with no solution.
We found a solution with a fairly good approximation using the data from the optical dilatometer.One of the advantages of measuring the thermo-mechanical behaviour of a glass specimen using a non contact dilatometer is the fact that it is possible to get a reliable measurement of the expansion of the glass for a wide temperature range above the glass transition temperature (Tg) . Above the Tg the glass enters in the supercooled liquid state and then in the liquid state. The very high increase in the slope of the curve after the Tg is due to the higher degree of freedom of the structural units, and this is indeed the expansivity of the molten glass. The curve measured with the optical dilatometer reaches a point of maximum and the starts falling down. Since the measurement is carried out with no contact with the specimen, there is no external force applied to the glass. The glass specimen is becoming shorter because the surface tension of the glass is pulling the specimen tips, making them round. The volume of the glass is still increasing, but the length of the sample is shortening because it is becoming rounded.

Fig 4: samples of glass before and after the measurement with MISURA LT optical dilatometer.

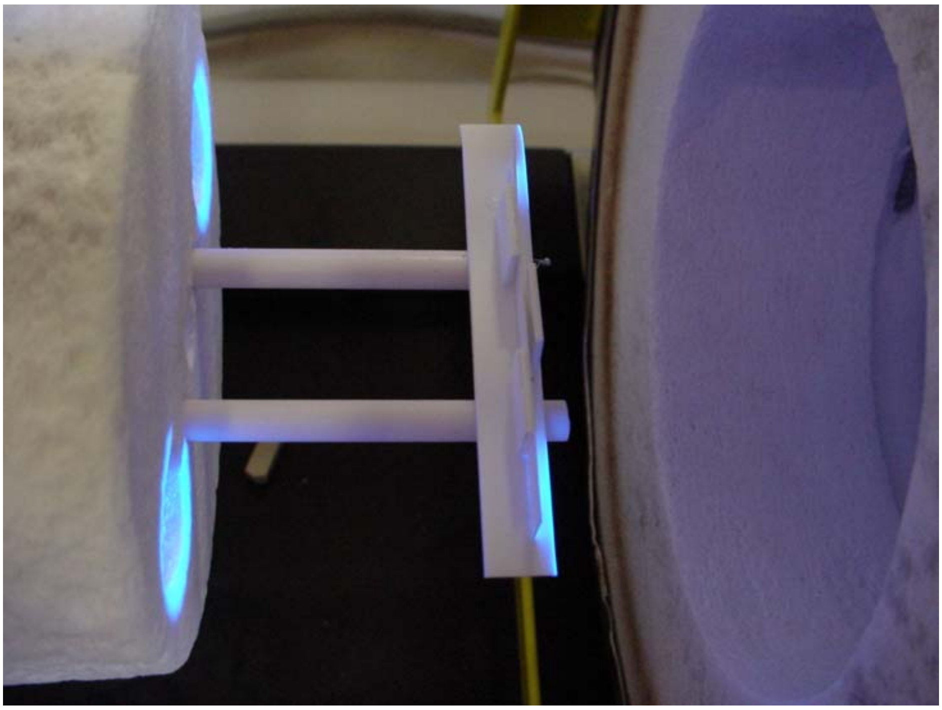

Fig 5: The measuring system of the optical dilatometer.

In order to get an estimate of the density at high temperature we derive the equation of the line passing through two points in the straight segment of the curve above the Tg.
This line is extrapolated up to the desired temperature to know the value of the increase in volume. Since the mass of the sample is not changed due to the temperature increase, it is then possible to know the density at the given temperature.

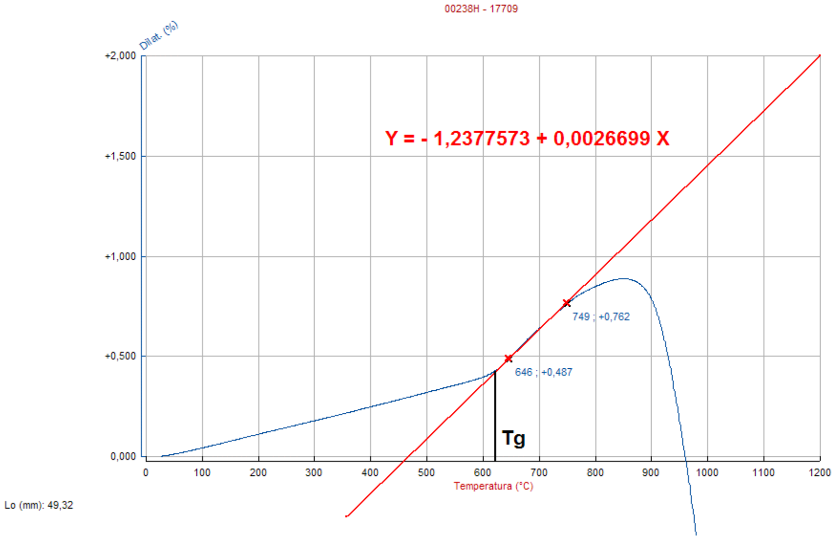

Fig 6: Extrapolation of the expansion of a liquid glass above the transition temperature.

In the shown example the extrapolated expansion at 1200 °C is 1,9661 %.
The density of the glass at room temperature was 2243 Kg/m^3 and then the extrapolated density at 1200 °C will be 2115,73 Kg/m^3.Of course, if the user has available a better estimate of the density at the temperature of the measurement, he can input the true value.

The measurement of surface tension

The actual measurement of the surface tension is carried out analysing the profile of the drop, and the heating microscope MISURA 3 is the ideal instrument to look inside a kiln at high temperature.

The first picture is an image of a soda lime glass drop at 1100 °C over a platinum foil. The drop of glass is crystal clear and the light spot in the centre is due to the lens effect of the glass. The calculated surface tension is 346 x 10^{-3} N/m, which is good agreement with reported data.

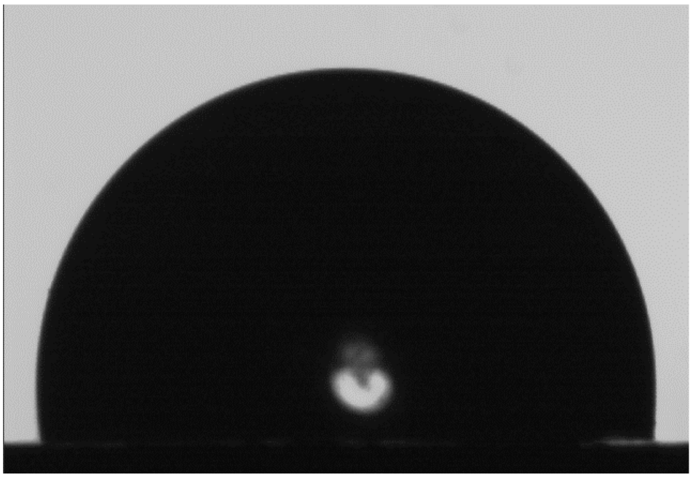

Fig 7: image of a drop of crystal clear soda-lime molten glass at 1100 °C, obtained with the heating microscope MISURA3

The second example is a drop of unoxidized molten solder (63% tin, 37% lead) in a nitrogen atmosphere at 200°C. In this case the calculated surface tension is 482 x 10^{-3} N/m, which, again is in good agreement with tabulated data.

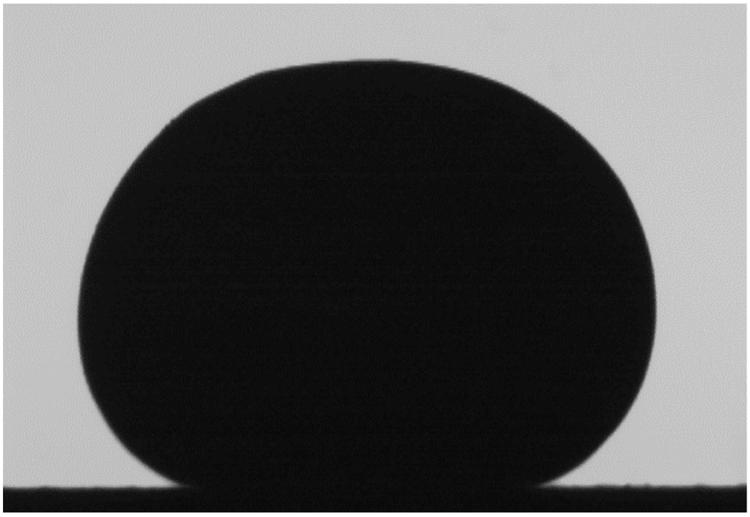

Fig 8: image of a drop of molten solder over an Alumina plate, in Nitrogen atmosphere obtained with the heating microscope MISURA 3.

The measurement is quite easy and fast, but it require a *good* sessile drop. One of the assumption of the measurement is the fact that the drop has an axial symmetry. If the image of the drop looks asymmetrical it is a waste of time to go ahead with the measurement. It is better to start a new test from the beginning, taking care to use a very clean specimen holder and a very well prepared starting sample.

Conclusions

The availability of a new instrument which makes easy and reliable the measurement of surface tension on molten material at high temperature gives a new research tool to the scientific community. The heating microscope is a very rugged laboratory tool and it does not require a lot of experience to be used. The addition of this feature broadens the field of use of this old laboratory technique.