

Falling Sphere Viscometry in Gravitational and Magnetic Fields**

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The classical falling sphere method based on *Stokes'* law is well known. Using gravitational forces, however, restricts the range of measurements considerably. This advantage can be overcome by applying iron spheres in a magnetic field, which allows to measure polymer melts with viscosities up to $\eta_0 = 10^9$ Pa s (with very strong magnets available even more). A special measuring cell designed for application in the magnetic field is tested with several silicon oils in the gravitational field too. In both cases wall and end corrections to *Stokes'* law have to be considered and are of main concern. Another important point is a reliable temperature measurement. Results especially for the high viscosity region of polymer melts are given.

(Keywords: *Falling spheres; Gravitational fields; Magnetic fields; Polymer melts; High viscosity*)

Viskosimetrie mittels fallender Kugeln im Schwerfeld bzw. magnetischen Feld

Die klassische Kugelfallmethode, basierend auf dem *Stokes'* schen Gesetz, ist gut bekannt. Im Schwerfeld ist der Meßbereich allerdings nicht sehr groß. Dieser Nachteil läßt sich durch die Verwendung von Eisenkugeln in einem Magnetfeld vermeiden, wodurch auch Polymerschmelzen mit Zähigkeiten bis $\eta_0 = 10^9$ Pa s gemessen werden können (mit sehr starken Magneten noch viel mehr). Eine spezielle Meßzelle für die Verwendung im Magnetfeld wird mit verschiedenen Silikonölen auch im Schwerfeld getestet. In beiden Fällen liegt das Hauptinteresse bei der Anwendung von Wand- und Endkorrekturen auf das *Stokes'* sche Gesetz. Ein weiterer wichtiger Punkt ist eine verlässliche Temperaturmessung. Ergebnisse speziell für das Gebiet großer Zähigkeiten von Polymerschmelzen werden angeführt.

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Introduction

To move an iron sphere, an inhomogeneous magnetic field has to be provided. The velocity of said sphere must be measured quite accurately. For that purpose a laser beam with a photoresistor as the detecting element is used. Details about the magnetic field and the arrangement to follow the position of the sphere are published elsewhere [1].

Measuring Cell

In this work main emphasis is given to the design of the measuring cell which has gone through a considerable change since our first model [1]. In constructing the cell two points we were concerned about most, are: easy handling during measurements and very reliable temperature distributions especially along the path of the moving sphere. The following example (polystyrene H 165) illustrates that very impressively:

$$\eta_0(180\text{ }^\circ\text{C}) = 91\,000\text{ Pa s and } \eta_0(182\text{ }^\circ\text{C}) = 72\,200\text{ Pa s}$$

That means a temperature change by approximately 1% is followed by a viscosity change of almost 10%. This relationship is pronounced even more at lower temperatures (and higher viscosities). Our first cell was basically a brass cylinder, its axis lying in the axis of the magnetic field and connected to a handle. It could be rotated by 180 degree (if the electromagnet, which is very heavy, is not turned around, the cell has to be turned to start the sphere at the same position after each experiment). The brass cylinder included a glass cylinder with the polymer melt inside. Due to the glass cylinder the cross section of the laser beam becomes distorted and, if the beam does not cross the cylinder symmetrically, is deflected and not even detected by the photoresistor sometimes. Originally temperature was measured by two thermocouples within two small brass cylinders connected with lids on both sides of the cylinder (Fig. 1). The positions of the thermocouples being above and below the axis of the cell. The average of such a pair of values was taken as the measuring temperature. Since the temperature difference within such a pair sometimes was as high as 8 °C (in all cases the temperature of the upper thermocouple was higher than in the case of the lower one, thermal convection being the probable reason) and considering the strong correlation of temperature variations to viscosity changes there may be results not good enough at least for certain purposes. After several attempts measuring the temperature at various positions and using other heating elements (we used a heating jacket in our first model), we have found a solution which combines easy handling with reliable temperature values.

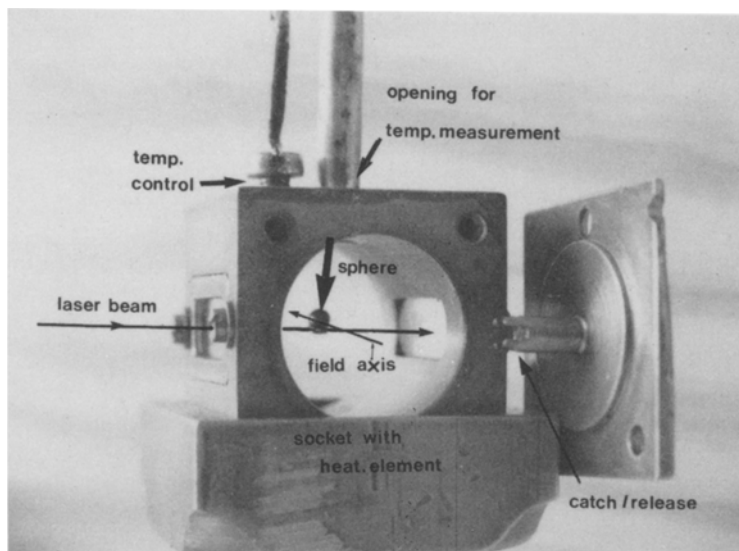
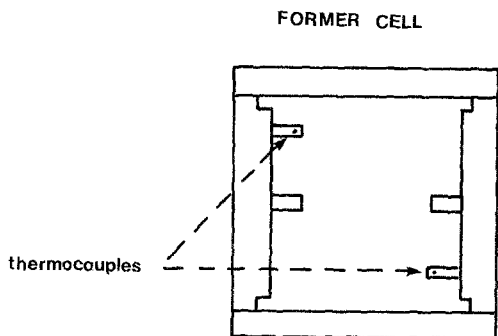


Fig. 1. Measuring cell with direction of magnetic field axis and detecting laser beam

Experimental

The cell which is presented here has a fixed pedestal with a cylindrical heating element inside (220 V, 100 W), it ends in a rectangular frame in which the proper cell fits exactly and can be fixed with a screw additionally. To allow the use of a cylindrical specimen which is yielded by our sample preparing device, the cell is simply a brass block with a circular boring. To avoid deflection of the laser beam two windows are inserted tangentially to the sample cylinder on both sides and vertical to the laser beam. Lids on both sides of the cell block carry cylinders along its axis which are necessary to release and catch the sphere during each experiment.

At the upper part of the cell there is an opening for temperature measurements directly in the polymer melt. After doing an experiment the next one can be performed by lifting the hot proper cell block out of the frame turning it 180° and inserting it again. With the help of heat conducting paste good thermal contact between brass block and pedestal (with the heating element) is provided. With the thermocouple immersed directly into the melt a very reliable temperature distribution can be measured and it turns out that near the center of the cell the temperature varies very slightly and reproducibly only (Fig. 2).

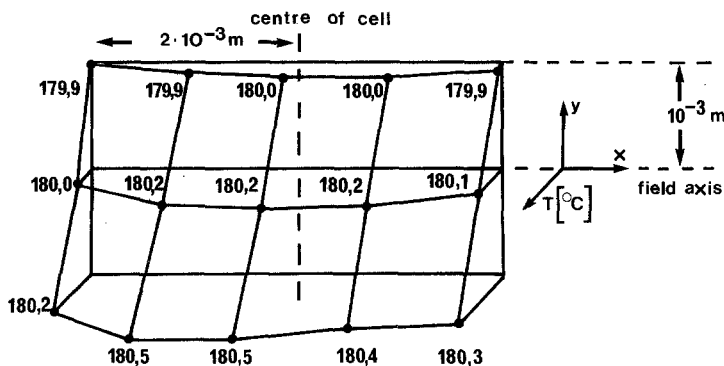


Fig. 2. Temperature distribution in the sample along, above and below the cell axis (magnetic field axis)

Corrections to Stokes' Law

As stated in the abstract already our method is based on *Stokes' law*. *Stokes' equation* assumes a sphere falling in an infinite liquid with no boundary and inertial effects [2]. As to the later ones in the case of polymer melts we are looking at, the stationary velocity v_s of the sphere is reached very fast, even with $\eta_0 = 10^3$ Pa s which is moderate for a polymer melt 98% of v_s is reached within 10^{-3} s $^{-1}$. Therefore only the boundary conditions have to be taken into consideration. Since the magnetic field and the force on the sphere depend strongly on the distance between the pole pieces (interfericum) this gap has to be comparatively small ($\sim 5 \cdot 10^{-2}$ m). Consequently, the distance over which the sphere can actually move is rather small ($\sim 2 \cdot 10^{-2}$ m) and so is the diameter of the sample. The wall corrections are very well established according to *Faxen* [3] and can be applied without checking them experimentally.

$$v_s \text{ (corrected)} = v_s \left[1 - 2.104 \left(\frac{d_{\text{sph}}}{D_{\text{cell}}} \right) + 2.09 \left(\frac{d_{\text{sph}}}{D_{\text{cell}}} \right)^3 - 0.95 \left(\frac{d_{\text{sph}}}{D_{\text{cell}}} \right)^5 + \dots \right]$$

$d_{\text{sph}} \dots, D_{\text{cell}} \dots$ sphere and cell diameter.

The effects of the boundaries on both ends of the cell are more open for discussion [4, 5]. Several authors (*Ladenburg, Lorentz, Tanner*) present cor-

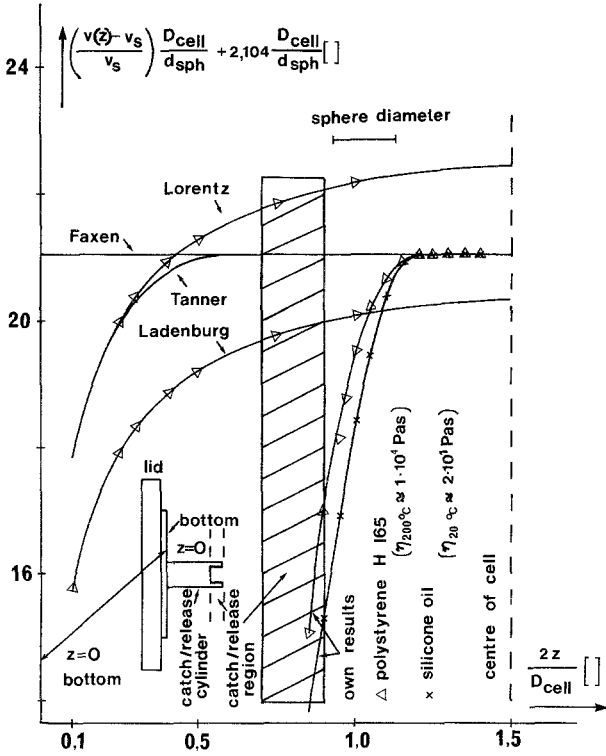


Fig. 3. Reduced sphere velocity $\frac{v(z) - v_s}{v_s} \frac{D_{cell}}{d_{sph}}$ plus first term of wall correction according to Faxen $2,104 \frac{D_{cell}}{d_{sph}}$ against reduced distance $2z/D_{cell}$ from the bottom of the cell. $v_s \dots$ velocity not depending on z (far enough from catch (release) cylinder); $v(z) \dots$ velocity depending on z [near catch (release) cylinder]

rections somehow different from each other. Therefore modifications necessary for the application of Stokes' law have to be determined experimentally, particularly since the lids of our cell are not plain but have a small cylinder in their center. To compare theory with experiment various silicon oils (99% of v_s is reached within 0.1 s) of well known viscosity are used besides polystyrene H 165. Measuring at several distances from the catch (release) cylinders show the region where end corrections can be neglected (Fig. 3). It can be seen that this region is the same for samples with very different viscosities [$\eta_0(200^\circ\text{C}) \approx 10^4$ for polystyrene H 165 and $\eta_0(20^\circ\text{C}) \approx 20$ for the silicon oil most fluid we used], the correction being slightly different only. To concentrate on end effects the experiments are started in the gravitational field which yields constant forces on the sphere over the falling distance (the magnetic forces vary slightly). Applying corrections to Stokes' law according to our experimental results, data obtained near the catch (release) cylinders could be used too (if necessary). The next step is to use a magnetic field

instead of a gravitational one. Basically the validity of *Stokes'* law has nothing to do with the kind of force acting on the falling (moving) sphere. In our apparatus, however, the magnetic forces vary slightly from the left to the right side of the cell. (A comparison of the gravitational and magnetic field data allows to calculate this variation.) This could be changed eventually by using other pole pieces. However, being interested mainly in data in the high viscosity region, the distance over which the sphere moves, is very small ($< 10^{-5}$ m, with bigger distances it would take too long a measuring time) and no measurable change of the magnetic force is observed.

Calibration

Another viewpoint is the geometry of our device. Whereas gravitation moves the sphere vertically, it is moved horizontally in our case and we need a force which counteracts gravitation therefore. The geometry of our magnetic field provides such a force automatically from a certain field strength on. At the field strengths we are using mostly for our measurements this magnetic force towards the axis of the magnetic field is much bigger than the gravitational force on the sphere. This in turn leads to velocities of the spheres in the horizontal direction which are higher than the ones in the gravitational field. Particularly velocities v_s , different by orders of magnitude, demonstrate a problem of more general dimension. In using silicon oils for calibration, which have viscosities much lower as can be expected for polymer melts, large errors can occur. The reason is, that calibrating step by step introduces errors at each stage which behave according to the law for the propagation of errors [6].

For example: $v_s(\text{m}) \simeq 10 v_s(\text{g})$.

$v_s(\text{m}), v_s(\text{g}) \dots$ velocities in the magnetic and gravitational field.

Using $v_s(\text{g})$ to calibrate the magnetic field, we have to compare both velocities, that leads to the following relationship

$$f[v_s(\text{g}) v_s(\text{m})] = C \frac{v_s(\text{m})}{v_s(\text{g})}$$

$x \dots v_s(\text{m}); y \dots v_s(\text{g}); C \dots$ constant

$$v_s(\text{m}) = v_s(\text{m}) \pm m_x$$

$$v_s(\text{g}) = v_s(\text{g}) \pm m_y$$

$$f_x = \frac{C}{v_s(\text{m})} \quad f_y = -C \frac{v_s(\text{m})}{[v_s(\text{g})]^2}$$

$$m = \sqrt{m_x^2 f_x^2 + m_y^2 f_y^2}$$

If $m_x = m_y$ equals 10% in both cases $m = C \cdot \sqrt{2}$ follows.

If the velocities are of the same order of magnitude $v_s(\text{m}) \simeq v_s(\text{g})$

$$m = C \cdot \frac{\sqrt{2}}{10}$$

To restrict the possible error in our example to the same magnitude the higher velocity $v_s(\text{m})$ has to be measured ten times as accurately ($\pm 1\%$ only).

To avoid these shortcomings, a new method compensating the magnetic forces by elastic ones, has been introduced [1]. Glass springs with elasticity moduli varying according to the magnetic force are fitted perfectly for that purpose (glass springs are used because the magnetic field would exert additional forces on a steel spring).

Results and Discussion

Viscosities of polymer melts depend on shear rates, therefore we have to measure at several velocities of the sphere to evaluate the viscosity-shear rate relationship and eventually extrapolate the zero shear-viscosity. As can be seen from our results on polystyrene H 165, only at the highest temperatures and the strongest magnetic forces which are available in our set up a shear rate (velocity) dependence of the viscosity can be observed (Fig. 4). Therefore in the case of low temperatures and high viscosities

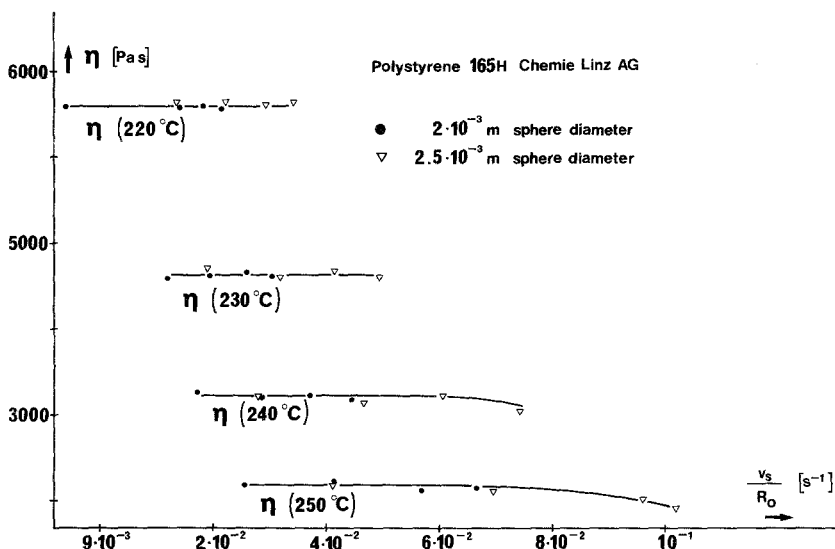


Fig. 4. Viscosity of polystyrene H 165 against shear rate $2v_s/D_{cell}$ at various temperatures

(very low sphere velocities), which is the most interesting region, there is no shear dependence of η whatsoever, we are measuring η_0 . In any case the limits of the range of our new method are set by the following points:

The accuracy, with which the support (carrying the detecting system with laser and photoresistor) can be positioned (shortest measuring distance 10^{-5} m).

The time needed for the sphere to move over the shortest distance possible, depends on the special kind of polymer and its degradation time finally. Because of practical reasons one may not wait more than ten hours, however.

As mentioned in the introduction already, the viscosity-temperature dependence, especially at lower temperatures, is a very strong one.

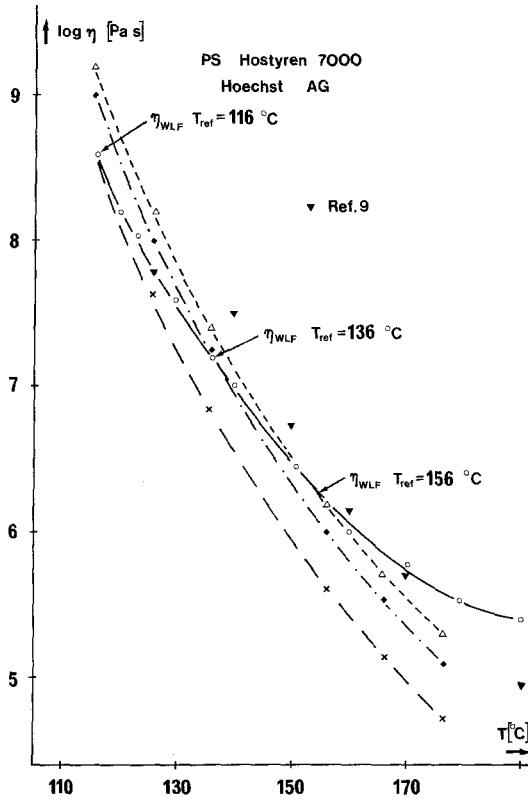


Fig. 5. Zero viscosity η_0 against temperature of polystyrene Hostyren N-7000 (Hoechst) compared with data calculated from the *WLF* equation

Therefore temperature measurements have to be done very exactly.

Finally we compare our results with the *WLF* equation [7]

$$\log\left(\frac{\eta}{\eta_{T_g}}\right) = \frac{17.4(T - T_g)}{51.6 + (T - T_g)} \quad (T_g = 66^\circ\text{C} \text{ according to Schwarzl [8]})$$

which is valid around the glass temperature (Fig. 5). To compare our results with the theoretical values we make several attempts with different reference temperatures (at T_{ref} we assume $\eta_{WLF} = \eta_{T_{ref}}$). Deviations may be due to the fact that the constants in the *WLF* equations are not universal ones [8]. To discuss these deviations more detailed, measurements on different polystyrene samples would be necessary. This will be done in the near future.

The main purpose of this paper was rather to present a new method to measure high viscosities and discuss its advantages and limits.

References

- [1] *Sobczak R* (1986) *Rheol Acta* (in print)
- [2] *Lamb H* (1945) *Hydrodynamics*. Dover, New York, pp 602
- [3] *Faxen H* (1923) *Ark Matematik Astron Fys* 17: 1
- [4] *Tanner RI* (1963) *J Fluid Mech* 17: 161
- [5] *Sutterby JL* (1973) *Trans Soc of Rheology* 17(4): 573
- [6] *Baule B* (1979) *Die Mathematik des Naturforschers und Ingenieurs*, part I, vol II. Verlag Harri Deutsch, Frankfurt, pp 9
- [7] *Billmeyer FW* (1971) *Textbook of Polymer Science*. New York, Wiley Interscience, London, pp 210
- [8] *Schwarzl FR, Zahradnik F* (1980) *Rheol Acta* 19(2): 137
- [9] *Pfandl W, Link G, Schwarzl FR* (1984) *Rheol Acta* 23(3): 277