Rheometric Study of Apparent Wall Slip in Microdispersions

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ABSTRACT

Rheometric evidence of the apparent wall slip (AWS) effect is the main subject of this paper. It is necessary, to treat together primary viscometric data from viscometric configurations with different hydraulic radii (e.g. different gap thickness *h*). The simultaneous using of several configurations is the feature which distinguishes a classical viscometry from the AWS viscometry. Three various sensors for the AWS rotational viscometry are considered here.

Two conventional sensors – coaxial cylinders (ZZ) and parallel plates (PP) – are compared with a novel sensor, the coaxial Morse-cone (KK), which seems to be most suitable for the viscometry under AWS effect. The related viscometric theory, based on two material functions – for fluidity and slip - is implemented to the PC software *AWSWork*, which supports the joint treating of primary viscometric data from different sensors.

A special statistical treatment – so called *local filtering* - provides the final results in a parameter-free form and provides some reasonable error estimates of the related material functions. The suggested approach is illustrated by the data on AWS rotational viscometry of an aqueous polymer solution and several concentrated aqueous clay suspensions.

INTRODUCTION

Colloidal suspensions, emulsions, and solutions containing nano- or microparticles are traditionally called microdisperse liquids. In addition to their non-Newtonian behaviour in bulk flow, the microdisperse liquids display anomalous flow behaviour close to solid walls. One important feature of this behaviour can be interpreted as apparent wall slip that, according to Mooney[1], "*…may be in reality an abnormally large velocity gradient in a thin layer adjacent to the wall, but can be treated mathematically as a discontinuity in velocity*".

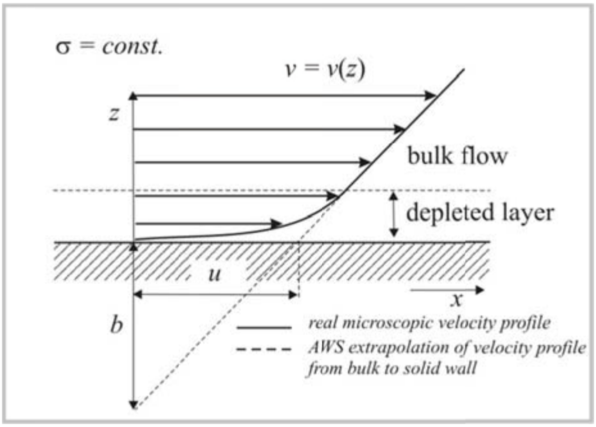

Figure 1. Apparent slip of microdisperse liquid adjacent to a solid wall

This intuitive concept of the apparent wall slip (AWS) has been formalized for a class of viscometric flows by Oldroyd[2], who in fact considered the apparent slip velocity *u*, see Fig. 1, to be an additional viscometric material function, $u = u[\sigma]$, common for all viscometric flows. Anyway, the analytic theory of general viscometric flows is presented in standard textbooks[3,4] with no relation to possible AWS effects.

As it is obvious from the extensive review by Barnes[5], a rational analysis of the AWS effects was long time limited to the idealized prototypes (e.g. Poiseuille[6] and Couette[7,8] flow), studied already by Mooney[1] and Oldroyd[2]. The AWS effects for PP configuration has been seriously analyzed only recently[8-10].

The real geometrical configurations in rotational viscometry differ from such idealized prototypes. Due to neglected geometrical non-ideality, commonly tackled as edge/end effects, the typical errors for Newtonian fluids in estimating shear stress from the primary data achieve 10–20%, see e.g. the report[11] on the standard ZZ configuration.

The errors in estimating shear rates may be even higher (above 100%) for pseudoplastic and viscoplastic materials. In other words: neglecting the AWS effect may completely misinterpret the viscometric data. An attempt to build up a rational basis for downstream treatment of primary viscometric data has been undertook in an extensive experimental study of the AWS effect[12-15]. Using KK sensor with adjustable gap thickness as an experimental technique and an advanced data analysis, it is possible to determine, with relative errors below 20%, even weak AWS effects that affect the primary readings (torque, rotation speed, geometry) by less than $\%AWS = 10\%$.

The AWS effect is often taken as an undesirable side effect. Some approaches[5,6,8] aimed to eliminate an AWS effect.

Another approach aims, so called AWS viscometry, aims at quantitative evaluating of both the bulk fluidity and the (apparent) wall slip. Such the approach, requires to perform measurements with at least two different hydraulic radii (gap thickness h) over a suitable range of shear stress σ.

METHODOLOGY

AWS concept

In analogy to other phenomenological concepts in fluid mechanics (interfacial tension, interfacial viscosity), also AWS effect can be described by modifying the boundary conditions of the continuum mechanics model, i.e. by introducing the concept of apparent slip velocity, u. This concept is illustrated in Fig. 1 for the simplest prototype of shear flows, but it can be applied in a consistent way for any viscometric flow[6-15].

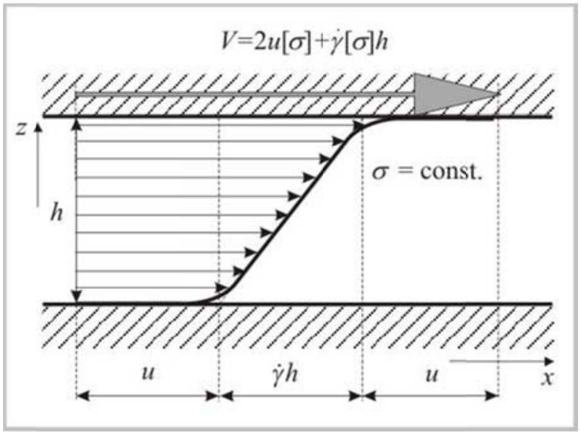

Figure 2. The concept of apparent wall slip velocity u for the longitudinal flow between two parallel plates (Simple shear prototype)

The overall kinematic effect is the sliding velocity V of the upper plate. When neglecting the thickness of an anomalous layers, adjacent to the walls, the overall effect can be visualized as a sum of the bulk flow and wall slip contributions:

$$V(\sigma, h) = G(\sigma, h)h = \dot{\gamma}[\sigma]h + 2u[\sigma]. \quad (1)$$

On a macroscopic level, the process is characterized by two material functions, bulk viscosity function $\dot{\gamma}[\sigma]$ and apparent wall slip velocity $u[\sigma]$, which are often represented by the corresponding fluidity and slip coefficients,

$$\dot{\gamma}[\sigma] = \varphi[\sigma]\sigma, \quad (2)$$
$$u[\sigma] = \chi[\sigma]\sigma. \quad (3)$$

Instrumentation

The bulk flow and wall slip effects can be distinguished only if a set of primary viscometric data is obtained for a series of the geometric configurations with various effective gap thickness *h*. In addition, the primary data for each *h* must cover the same range of characteristic wall shear stress σ. The standard shear-stress controlled rotational viscometers can be employed when using proper kinds of the sensors, see Fig. 3 and Fig. 4.

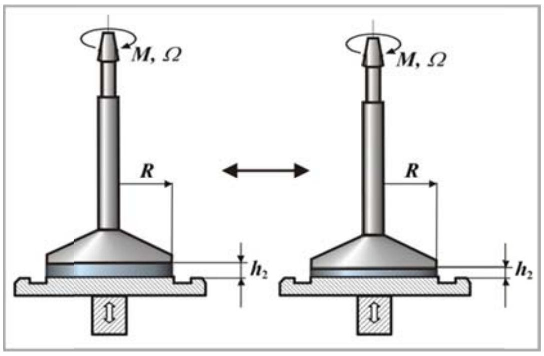

Figure 3. Parallel plate (PP) sensor

Parallel plate (PP) sensor in combination with a modern viscometer, allowing axial shift, gives a possibility of changing the gap thickness *h* without sample refilling. Unfortunately, strong edge effects[9,10], accompanying the measurements, are disqualify this configuration for a routine use of this geometry.

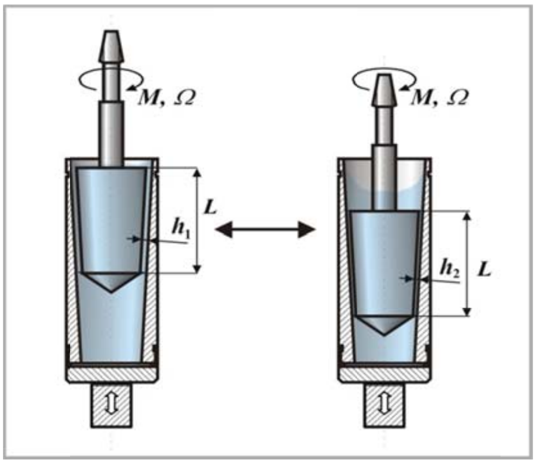

Figure 4. Sensor of coaxial Morse cones (KK)

A novel (KK) sensor with coaxial Morse cones, developed in our laboratory, combines the advantages of both coaxial cylinders (controllable edge effects) and parallel plates (variable gap thickness). When using this sensor in a modern rotational viscometer, an automated gap thickness adjustment is provided with no need to refill sample, as well as a good temperature control. Anyway, a careful calibration of the viscometers and viscometric sensors, via measurements with Newtonian fluids, is necessary[8,10] to adjust the gap thickness *h* with an acceptable accuracy.

Data treatment

Primary data of AWS viscometry are angular speed Ω, torque *M* and the sensor geometry, in particular an effective gap thickness *h*. The commonly suggested approach[14] of treating such the primary data is a smoothing and interpolating the data with respect to wall shear stress σ, and then a differentiation with respect to *h*. The partial differentiation process must be combined with an interpolation over the set of primary data and the result often displays an unacceptably large scatter of the constitutive information about slip velocity *u*. Alternative approach to data treatment is *local filtration* based on parametric representation of the constitutive information, by introducing empirical models for fitting the slip velocity and viscosity function. The process of local filtration has been developed for system of coaxial cylinders[14] system of parallel plates[15] and system of Morse cones[8,9] and its application to the data treating software *AWSWork* has been made. Calibration constants of used viscometer, geometry parameters of used sensors and primary viscometric data makes up complete set of necessary information for evaluating apparent wall slip effect.

EXPERIMENTAL

Aqueous dispersions of welan gum and kaolin have been tested and AWS effect has been evaluated.

All the available ZZ, PP and KK sensors were used for measurements of the welan gum sample. The kaolin suspensions, which display rather viscoplastic behaviour with severely changing fluidity, were tested only in a KK sensor.

Sample preparation

Aqueous welan gum solution of 2%wt concentration was prepared by solving of the polymer powder in demineralized water. Resulting solution was gently stirred by a glass stirrer. Weak vacuum was applied to remove small dispersed bubbles. Few drops of 5% solution of phenol in ethanol were added to prevent biodegradation of the prepared solution.

The kaolin dispersions (samples K40, K40H, K35, K30 correspond to kaolin content of 40%wt, 35%wt and 30%wt) were prepared from kaolin *Sedlec 1a* (produced by Sedlecky kaolin a.s., Czech Republic) and demineralized water. The sample K40H containing was prepared with an addition of 0.15%wt sodium hexametaphosphate as a dispergator. In all the cases, demineralized water or solution of dispergator was added to dry kaolin and then the sample stayed for 2 days. Then they were treated in ultrasonic bath for 30min (40kHz, nominal acoustic power of 30 $kW.m^{-3}$) and finally evacuated.

RESULTS & DISCUSSION

Presented results can be divided into the two cases. First case is a class of methodic results where the common treatment of primary data from various viscometric sensors (ZZ, PP, KK) is documented. Second case is class of results obtained for the kaolin dispersions where the evaluating of AWS is possible only with the novel KK sensors.

Methodic results

Principal feature of the AWS viscometry is a measurement with at least two different *h*. Another option is to combine viscometric data from completely different types, e.g. PP, KK, and, possibly, ZZ. Only one data set from each viscometric sensor could be sufficient for AWS evaluation. Anyway, there is a risk of measurements with inadequate gap thickness and then AWS characteristics are not be reliably determined. Therefore, the experiments with more than one gap thickness for each viscometric sensor are recommended and combination of all registered data from all sensors is afterword applies.

Welan gum sample

The welan gum sample was tested on three types of sensors with eleven different gap thicknesses *h*. Results of common treatment are plotted in Figs. 5-7. Individual sensors are distinguished by symbol shape (KK ●, ZZ ◆, and PP ▲), different *h* by the gray intensity. It can be seen from Fig. 5 that the fluidity data are in a good agreement even for sensor ZZ with a large gap thickness, *h* = 1.69 mm.

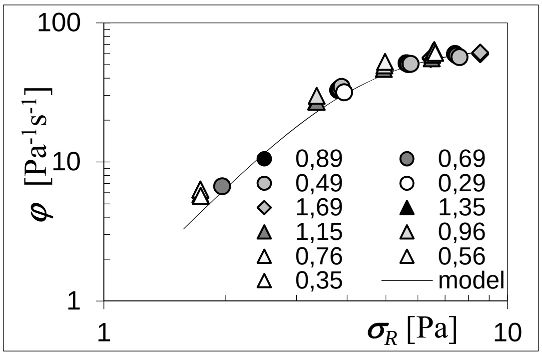

Figure 5. Fluidity of welan sample. The data for KK sensor are noted as circles ●, for Z40 DIN as diamonds◆, and for PP60 as triangles ▲. The numerical labels give the gap thickness *h* in mm.

Data on slip coefficient are rather scattered, see Fig. 6. It corresponds to the low level of AWS effect, occurring for the welan gum sample. A contribution of AWS to total kinematic effect is about $\%AWS$ = 30%, which is enough for detection but too low for a smooth data fitting.

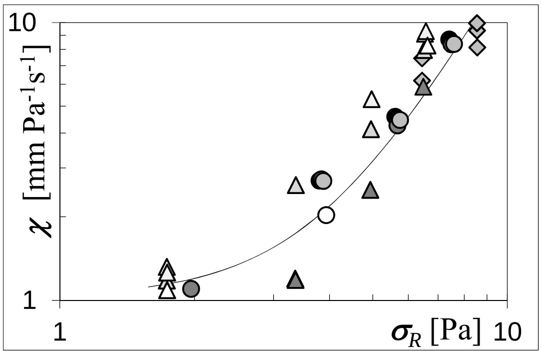

Figure 6. Slip coefficient of welan sample

Data of extrapolated slip length b (compare with Fig. 1) are affected by scatter of slip coefficient, because they are calculated as a ratio of slip coefficient vs. fluidity, see Fig. 7. When b is comparable with the gap thickness h, then AWS effect is necessary to take into account.

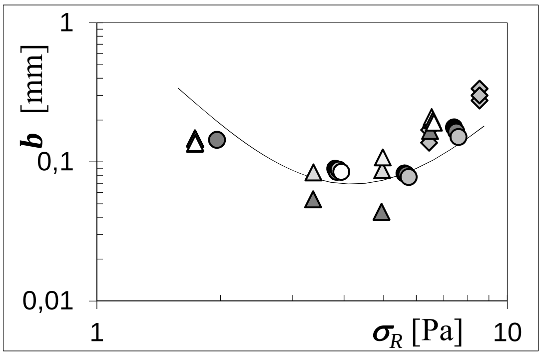

Figure 7. Extrapolated slip length as a function of wall shear stress

Kaolin samples

The aqueous kaolin dispersions are typical shear thinning (pseudoplastic or even viscoplastic) materials, widely used in ceramics or as a pigment in paper coatings. The fluidities of kaolin dispersions are very low and an additive is often used to increasing it (see fluidity of sample K40H in the Fig. 8). All kaolin dispersions data were measured with only KK sensor applying three gap thicknesses, h = 1.089 mm, 0.812 mm and 0.628 mm.

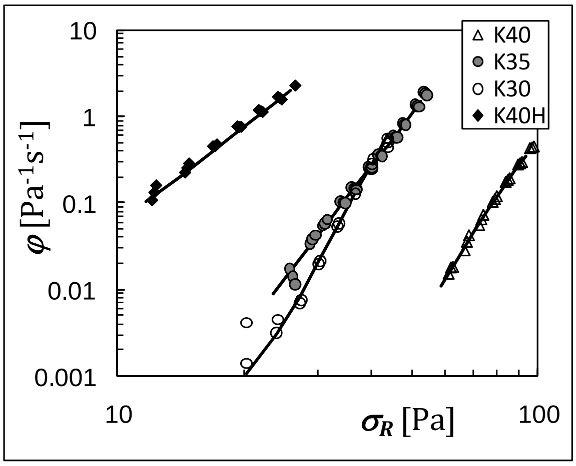

Figure 8. Fluidity of the kaolin dispersions.

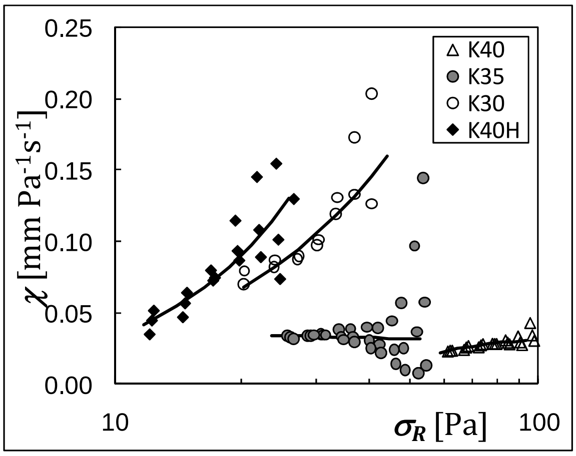

Figure 9. Slip coefficient of the kaolin dispersions.

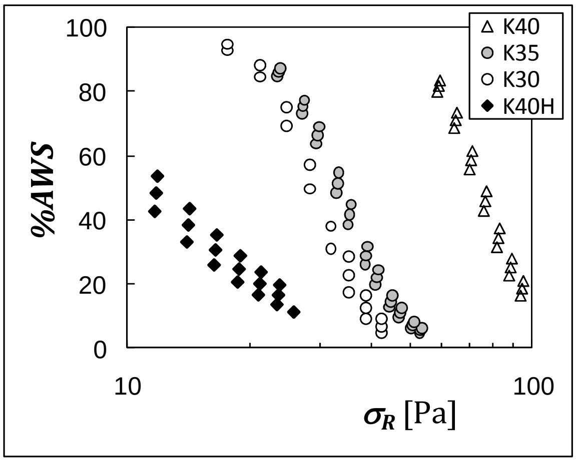

Figure 10. Contribution of AWS to total kinematic effect for kaolin dispersions for the three levels of gap thickness h.

Scatter of the slip coefficient, see Fig. 9, is wider in the range of higher shear stresses. There, the AWS effect is much weaker (below $\%AWS$ = 20%), see Fig. 10, because of severely rising bulk fluidity, apparent in Fig. 8.

The extent of AWS effect depends also on the gap thickness h. It can be seen in the Fig. 10, where a triple of points at the same shear stress σ corresponds to three aforementioned different gap thicknesses h. The highest point corresponds to the smallest gap. It is clear that the AWS effect influences flow mainly in narrow channels.

CONCLUSIONS

AWS rotational viscometry is discussed for three types of viscometric sensors. Aqueous solution of welan gum displaying a adequate AWS effect was chosen for demonstration of common approach to primary data treatment. Kaolin dispersions of various concentrations were tested on KK sensors for presence of AWS effect. Smooth data of slip coefficient with a little scatter at low wall shear stress, see Fig. 9, together with extremely high AWS contribution to total kinematic effect, see Fig 10, are evidence for AWS viscometry concept employment for such materials.

ACKNOWLEDGMENTS

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