Determination of liquid viscosity at high pressure by DLS

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Abstract. The movement of particles with a size smaller than few microns is governed by random Brownian motion. This motion causes the fluid to flow around the particles. The force acting upon Brownian particles as well as their velocities are measured by using the dynamic light scattering (DLS) technique. It provides the relationship between fluid shear stress and shear rate over the Brownian particle and determines the viscosity properties of the fluid. In this study, we propose a new rheometer which is widely applicable to fluid viscosity measurements at both normal and high pressure levels for Newtonian and non-Newtonian fluids.

1. Introduction
The ability to properly measure the viscosity of a fluid is crucial for a vast array of engineering and scientific applications. In general, fluid viscosity is measured during laminar flow at low Reynolds numbers. The viscosity of a Newtonian fluid is independent of the flow conditions and can be easily determined from the relationship between fluid shear stress and shear rate. However, the viscosity of non-Newtonian fluids fluctuates depending on the flow conditions and is therefore determined based on the relationship between fluid shear stresses and shear rates measured for different flow conditions. The fluid shear stress can be caused by moving an object such as a cylinder, disk or sphere inside the fluid. However, the application of this method becomes especially difficult in high pressure conditions.

The new rheometer proposed in the present study [1] is based upon Brownian motion of fine particles smaller than a few micrometers. The fluid shear stress and shear rate over the surface of a Brownian particle moving randomly in a fluid are measured by using a dynamic light scattering technique. The relationship between fluid shear stress and shear rate can therefore be obtained at different fluid flow conditions around particles of different sizes. This method can also be used to measure the viscosity of non-Newtonian fluids and constitutes a powerful method for measuring fluid viscosity at high pressures, as there is no need to insert moving objects in a stationary fluid. In the following sections, we will show the theoretical background as well as experimental results for a Newtonian fluid.

2. Experiment
Figure 1 shows the experimental diagram. The experimental equipment consists of a high pressure system and a DLS system. The high pressure system controls the pressure of the cell with a plunger pump and a pressure generator with a range of 1-4000 bar. Water is used as a pressurizing fluid. The high-pressure cell is equipped with four sapphire windows at right angles. A He-Ne gas laser with a
wavelength of 632.8 nm or a 405 nm violet laser is used as a light source. The laser beam propagates through the sapphire window and is focused at the center of the test cell in the high pressure cell. The scattered light then passes through the beam splitter, lens and pinhole, after which it is detected by a photo-multiplier (PMT) converting the optical signal into an electronic signal. The angle between the incident laser beam and the scattered signal is normally $90^\circ$ in order to position the measurement point at the center of the test cell. The evolution of the detected photon numbers in time is stored in the PC memory by using a special counter board. The minimum gate time and memory size of the counter are 50 ns and 64 M bytes, respectively.

3. Diffusion coefficient of Brownian particle

The time-averaged autocorrelation function of photon number for monodisperse particles as measured using the aforementioned optical system is given by:

$$G^{(2)}(t) = B(1 + \beta \exp(-2\Gamma t))$$

where $B$ is the baseline constant, $\beta$ the experimental constant and $t$ the delay time. The relaxation rate $\Gamma$ is directly related to the diffusion coefficient of Brownian particle as follows:

$$\Gamma = q^2 D$$

where $q$ is related to the wavelength $\lambda$ of laser light, the scattering angle $\theta$ and the refractive index $n$ of the fluid as follows:

$$q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right).$$

Hence, the diffusion coefficient of Brownian particle is experimentally determined by using the DLS method.

4. Fluid shear stress and shear rate

The force acting upon a Brownian particle is given by the Nernst-Einstein equation

$$F = kT u / D$$

where $k$ is the Boltzman constant, $T$ the absolute temperature, $u$ the average velocity of Brownian particle and $D$ the diffusion coefficient of Brownian particle. The average velocity of a Brownian particle is defined by

$$u = \sqrt{kT/m}$$

where $m$ is the mass of the Brownian particle. Hence, the shear stress ($\tau$) over the surface of the particle and the fluid shear rate ($du/dy$) are, respectively, given by

$$\tau = F / (\alpha \nu^2)$$

Figure 1 Experimental equipment.
1 High pressure cell
2 Pressure promoter
3 6-ways valve
4 Plunger pump
5 Water pressure media
6 Laser
7 PMT
PH: High pressure gauge
PL: Low pressure gauge
VH: High pressure valve
VL: Low pressure valve
VT: Top valve
\[
\frac{du}{dy} = \frac{u}{\alpha \tau}
\]

(7)

where \( r \) is the particle size. The diffusion coefficient of a Brownian particle \( D \) is obtained from the autocorrelation function of the change in the number of photons over time as the intensity of the light scattered from the particle being detected by photo-multiplier. If the radius of the particle is known, it is possible to obtain the relation between the fluid shear stress and the shear rate from the diffusion coefficient of Brownian particle and to measure the viscosity of the fluid with DLS.

5. Results and discussion
The shear stress and shear rate over the surface of Brownian particle are measured with DLS and determined using Eqs. (6) and (7). The relationship between shear stress and shear rate of pure water at atmospheric pressure is shown in Fig. 2 along with measurements obtained with a normal rotational viscometer. It is obvious from the plots that the data obtained with the two methods are linearly correlated and are in good agreement. This allows us to conclude that the fluid shear stress and shear rate around a Brownian particle can be determined by using the method proposed in the previous section with the accuracy to \( \pm 5\% \). Hence, the viscosity of a Newtonian fluid is given by the gradient of the correlated line, as shown in Fig. 2.

![Figure 2 Relationship between fluid shear stress and shear rate for pure water at atmospheric pressure and 298 K.](image)

Moreover, this method is especially suitable for measuring the viscosity of fluids at high pressure, as it does not require an object to be moved inside the fluid. Here, pure water and an ethanol-water mixture are used as test fluids. The viscosity of the ethanol solution is higher than that of pure water, and it decreases as the temperature increases. The maximal viscosity of the ethanol solution as a function of
the ethanol concentration is reached at 20 - 30% of ethanol content. Tanaka et al. [2] reported the specific volume and viscosity of ethanol-water mixtures at high pressure by using a falling-cylinder viscometer. Figure 3 compares our data obtained by using the DLS method with the data from [2]. In [2], Tanaka et al. measured the viscosities of water and a 20 mol% ethanol solution at pressures up to 785 bar. The viscosity of water is almost constant in the range of 1-4000 bar, although it is sensitive to the temperature. On the other hand, the viscosity of the 20 mol% ethanol solution increases proportionally to the pressure. As shown in Fig. 3, the data obtained using the DLS method agrees well with the results from [2] over the common measurement range of pressures up to 785 bar. The dependence of the viscosity of the ethanol-water mixture on the pressure increases at higher temperatures.

![Viscosity of pure water and ethanol-water solution against pressure.](image)

6. Conclusion
A new method for measuring fluid viscosity proposed in the present paper is based on the dynamic light scattering (DLS) technique. One of the advantages of this method is its ability to determine the relationship between the fluid shear stress and shear rate over the surface of Brownian particles. Hence, the method is applicable in measurements of the viscosity of non-Newtonian fluids. The DLS technique allows for the viscosity of fluids in stationary conditions to be measured without using a moving object in the fluid. We apply this method to perform a simple measurement of the viscosity of fluids in high pressure conditions. Using our method, we measured the viscosity of an ethanol-water mixture at pressures up to 4000 bar. The results show that the viscosity increases linearly as the pressure increases, which is in good agreement with previously obtained results.

References
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