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Sheared liquids explored by means of neutron scattering

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Abstract
Despite its large economic impact, lubrication has not been well understood up to now. The present paper shows the possible impact of quasielastic and inelastic neutron scattering in this field. Liquids under shear have been investigated using the backscattering instrument IN16 (ILL). Macroscopic and microscopic modes, which can be addressed within the same measurement, have been explored. For a commercial motor oil a macroscopic velocity distribution with surface slip has been found. For a polymer solution (P85 in deuterated water) we report diffusion to slow down under shear. Additionally, diffusion becomes anisotropic under shear for both samples. The experimental data are evaluated quantitatively by using computer simulations which show the limitation of this technique: the quasielastic linewidth should not be larger than the inelastic energy shift from Doppler scattered neutrons.

1. Introduction

Our present understanding of lubrication, in particular on an atomic length scale, is still marginal in spite of its large economic impact. It is estimated that about 6% of the gross national product of the USA is lost due to friction and wear [1]. One reason for this lack in understanding relates to the difficulty of observing the behaviour of a liquid confined to a narrow slit in between two moving components made from opaque material. The high power of penetration of neutrons into many engineering materials and the large incoherent scattering cross-section of hydrogen, contained by most liquid lubricants, however, lead to the possibility of accessing information on lubricant dynamics even under application-relevant conditions. Recently, we have initiated a study of liquids under shear employing several neutron scattering techniques and it has been shown that macroscopic flow of lubricants can be observed by means of neutron backscattering [2]. However, the plate–plate-type shear device used for this early measurement did not meet the special requirements of neutron

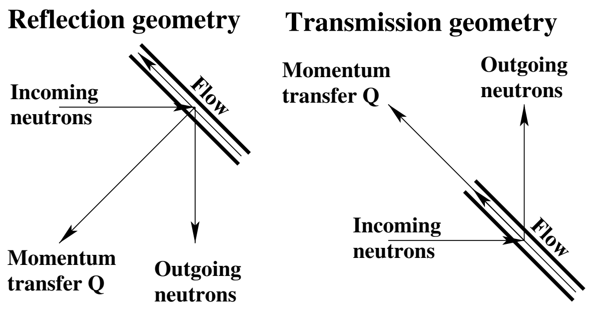

Figure 1. Scattering geometries for the dynamic scattering experiments on liquids under flow.

backscattering. To allow a more detailed investigation, a special type of plate–plate shear device has been built, optimized to study the dynamics of liquids by means of quasielastic and high-resolution inelastic neutron scattering [3]. With this device it has been possible to distinguish qualitatively between different velocity profiles of sheared liquids and to monitor first indications for changes in microscopic liquid dynamics on an atomic length scale [3, 4]. From the present work a quantitative description of these changes becomes possible. Further surface slip has been found for a commercial motor oil when sheared at 18 °C. Additionally, within the same experimental set-up it has been possible to monitor a change from isotropic diffusion in the unsheared sample to anisotropic motion under shear on a length scale of 1.4 $Å^{-1}$ and for the microelectron volts energy regime.

2. Experimental details

2.1. Neutron backscattering

High-resolution neutron backscattering makes it possible to acquire information about the macroscopic flow of a liquid and to obtain within the same measurement information about diffusional processes within the sample. The high energy resolution of less than 1 μeV is achieved by employing Si(111) crystals set in the backscattering geometry both as monochromator and analyser. To scan for different energies, the neutron velocities are modified by the monochromator crystals mounted on a Doppler drive. The speed of the Doppler drive is up to 2.5 m s^{-1}, quite similar to the speed which can be obtained with the shear apparatus. A more detailed description of the instrument IN16 (Institut Laue-Langevin, ILL) at which the current experiments were carried out is given elsewhere [5].

For dynamic measurements with liquids under shear, two different scattering geometries have to be considered as shown in figure 1. In reflection geometry with the vector of momentum transfer Q perpendicular to the flow, only microscopic diffusion in the direction of the shear gradient can be studied. Turning to transmission geometry with Q parallel to the flow, in addition inelastically Doppler scattered neutrons from the macroscopic flow become visible.

2.2. Sample

Two different samples have been studied. First a commercial motor oil ANTAR was chosen, which represents a system with direct relevance to lubricant application. As a second sample a 33% (by weight) solution of the surfactant P85 was studied. The structural properties including unimer, cubic and lamellar orderings of P85, are well known from SANS [6] investigations for

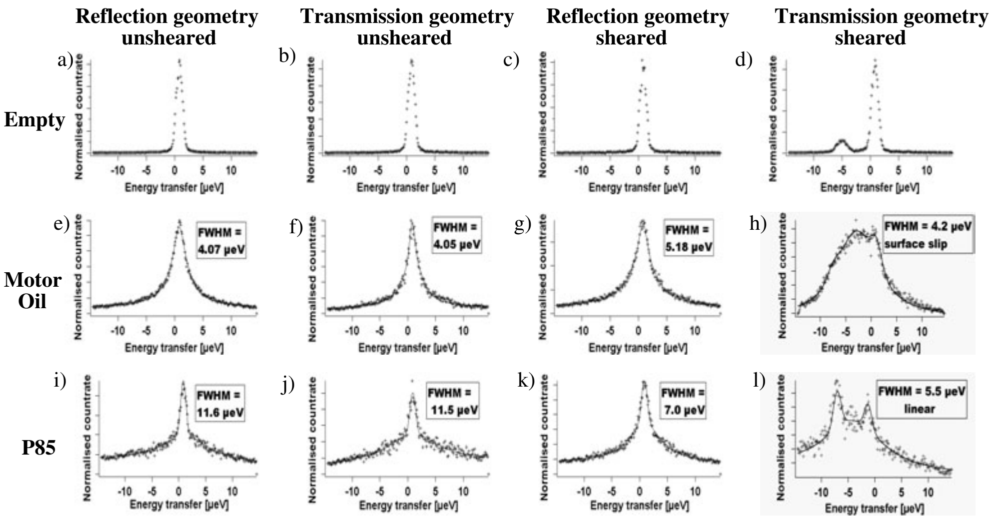

Figure 2. High-resolution backscattering data obtained at IN16 (ILL). The first row, (a)–(d), shows spectra for the empty shear device, the second one, (e)–(h), spectra for a commercial motor oil and the third, (i)–(l), spectra for a polymer solution of P85 (33% by weight) dissolved in deuterated water. A detailed description of the spectra is given in section 3.

different concentrations in water and over a wide temperature range. In addition, a previous reflectivity study has shown that the sample is very sensitive to shear. The lamellar ordering becomes enhanced when a hydrophilic-coated silicon wafer is used as wall material in the shear device while it is destroyed for a hydrophobic coating under shear [3].

3. Experimental results

Figure 2 presents high-resolution backscattering measurements conducted at IN16 (ILL). The first row, (a)–(d), shows data for the empty cell with the aluminium discs covered by a strong elastic scatterer (sticky tape) to determine the instrumental resolution to 1.2 μeV. The three panels (a), (b), (c) in the top row show data with both discs stationary in transmission and reflection geometry and with one disc set into rotation in reflection geometry. As expected, there is no difference visible, implying that only elastic scattering from the discs is visible. However, in transmission geometry and with one disc rotating, an additional inelastic peak from Doppler scattered neutrons appears at -8.5 μeV corresponding to a disc speed of about 1.8 m s^{-1}. This second peak is broader than the elastic line due to the velocity gradient from the finite beam size of about 2.5 cm for a disc radius of 9 cm. The difference in intensity of the two peaks arises from the different amounts of tape glued onto them and has no further relevance for this experiment. The second row of panels, (e)–(h), in figure 2 shows the results for the cell filled with the motor oil at a disc spacing of about 0.3 mm in the same scattering geometries as the corresponding upper panels. The elastic line in the first three panels, (e)–(g), becomes quasielastically broadened due to diffusion processes in the sample. The two spectra taken without shear in transmission and reflection geometry, (e), (f), show similar linewidths of $2\Gamma = 4.07$ (FWHM) and $2\Gamma = 4.05$ μeV, meaning a diffusion constant of 3.1×10^{-7} cm^2 s^{-1}, calculated from Fick's law for random jump diffusion ($D = \Gamma/(\hbar Q^2)$ with $\hbar = h/(2\pi)$ and h the Planck constant). For the sheared sample (shear rate 6000 1 s^{-1}) in reflection geometry, (g), with Q perpendicular to the flow, the quasielastic line clearly broadens to about $2\Gamma = 5.18\ \mu$eV ($D = 3.9 \times 10^{-7}$ cm^2 s^{-1}) indicating an acceleration of the diffusion modes in the direction of the shear gradient in the dynamic region investigated and for a momentum transfer of $Q = 1.4$ Å^{-1}. In the fourth panel of the second row, (h), the inelastic scattering reflects directly the velocity distribution of the sample between the discs. To interpret this spectrum the data have been fitted by a scattering law described in section 4. The best fit has been obtained for a Lorenzian linewidth of $2\Gamma = 4.2\ \mu$eV, which is quite similar to the value found for the sample at rest. This means that diffusion becomes anisotropic upon application of an external shear force. The fitted velocity distribution has lower and upper limits of 0.15 and 0.70 times the velocity of the rotating disc, respectively, with a linear increase between these two boundary values. This implies a non-Newtonian behaviour with a large internal friction within the liquid and a weak interaction at the solid–liquid interfaces, resulting in a pronounced surface slip at a temperature of 18 °C. The shear rate dependence of these dynamical changes will be addressed in future measurements. The third row in figure 2 shows spectra obtained with the sample of P85 dissolved in deuterated water for a disc spacing of 0.6 mm and a temperature of 18 °C. Again the first two spectra, (i), (k), show similar quasielastic linewidths of around 11.5 μeV ($D = 8.7 \times 10^{-7}$ cm^2 s^{-1}). Under shear (shear rate 3000 1 s^{-1}), this line narrows to 7 μeV ($D = 5.3 \times 10^{-7}$ cm^2 s^{-1}) in reflection geometry and 5.5 μeV ($D = 4.2 \times 10^{-7}$ cm^2 s^{-1}) in transmission geometry. This means that diffusion slows down in both directions in contrast to the case for the data on the engine lubricant in row 2. This general reduction of particle mobility may relate to the pronounced structural ordering that has been found earlier in reflectivity studies on P85 [3]. Nevertheless, we observe also in the case of P85 a transition from isotropic to anisotropic, as found for the motor oil. The large quasielastic linewidth and the insufficient statistics makes a calculation of the velocity distribution between the discs for this sample impossible. Panel (l) shows as an example a fit with a linear distribution including the scattering from the discs shown as a solid line.

4. Computer simulations

Computer simulations have been carried out to obtain a quantitative interpretation of the experimental results shown in figure 2. The contributions to the scattering function consider

(i) the molecular diffusion by Lorenzian line profiles which are convoluted with an assumed Gaussian instrumental resolution function [7],
(ii) a velocity distribution function for the inelastic part of the spectrum,
(iii) a velocity gradient for different disc radii and
(iv) a smearing of the Q-value according to the relaxed Q-resolution of the instrument.

The results are shown as contour plots in figure 3. The x-axis represents the energy transfer in units of the inelastic peak position from the rotating disc and the y-axis represents the quasielastic linewidth for the internal diffusion in units of the inelastic peak position. The greyscale represents the difference in scattering pattern which is shown as local percentage values. Panel (a) shows the difference in energy spectrum between a linear velocity distribution from the fixed to the moving surface and a velocity distribution with a surface slip of 50% at each boundary (this is equivalent to a liquid layer with no internal shear gradient). Panel (b) is a difference plot again, for a linear velocity profile characterized by 50% of the thickness of the liquid sticking to each boundary (equivalent to an infinitely steep gradient at a discontinuity point in the middle of the liquid layer). The velocity distributions that have been used for the calculation are also depicted in panel (d). The calculations show that it is more difficult to identify a linear velocity profile with surface slip (panel (a)) than a linear velocity profile

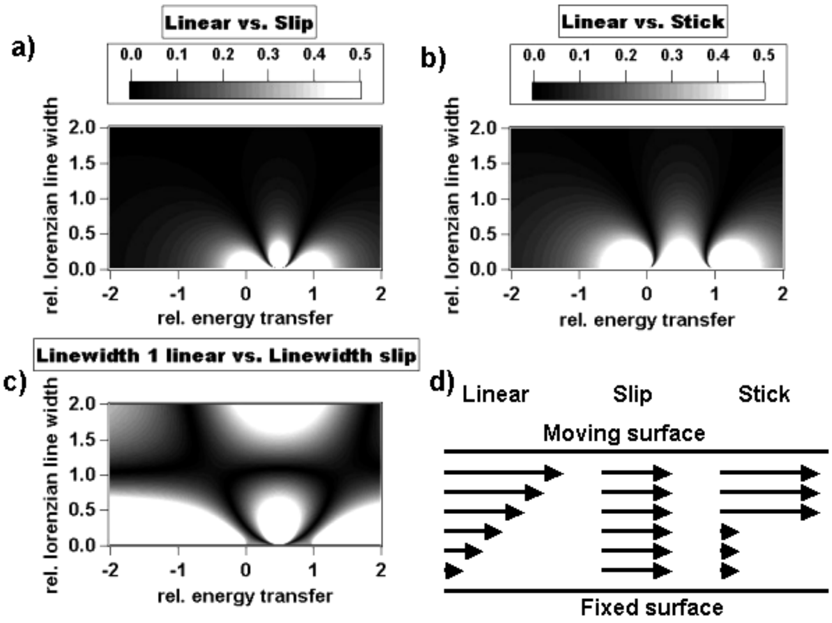

Figure 3. Contour maps of the difference in intensity distributions between simulated quasielastic spectra. The x- and y-axes are normalized to the position of the inelastic peak from the rotating disc. Panel (a) shows the comparison between a linear velocity distribution and one with surface slip and panel (b) shows the comparison between a linear velocity distribution and one with surface stick. The velocity distributions are illustrated in (d). The difference between the linewidth for a velocity distribution with surface slip and the linewidth, equal to the inelastic peak position, for a linear distribution is shown in panel (c).

with sticking layers (panel (b)). Nevertheless, for statistics with error bars smaller than 10% a distinction is possible if the quasielastic linewidth is not larger than the energy value of the inelastic peak position. Panel (c) shows the difference between a linear velocity distribution with a quasielastic linewidth of 1 (in units of the inelastic peak position) and a distribution with surface slip and quasielastic linewidths between 0 and 2. In these cases, the linewidths can be determined from the wings of the experimental spectra with an estimated error of 10%. This means that a macroscopic velocity distribution can be fitted to the spectrum of the motor oil—figure 2, panel (h)—with the Lorenzian linewidth half the value of the inelastic peak position. For the P85 solution with a linewidth larger by a factor of two, only microscopic diffusion can be quantified.

5. Conclusions

Neutron scattering has proven to be an excellent tool for the investigation of the dynamics of flowing liquids. Both the macroscopic velocity profile of the fluid and the atomic scale diffusion are accessible. High-resolution neutron backscattering from a sample of a motor oil showed a highly non-linear macroscopic velocity distribution with a pronounced surface slip. In addition, it has been shown that the microscopic diffusion modes become anisotropic under shear.

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