# MICROCANTILEVER RHEOMETER

**Technical Field of the Invention**

This invention relates to equipment for measuring the viscosity and/or density and other rheological properties of a fluid. Note that fluid refers to both gases and liquids. In particular it relates to a microcantilever rheometer. The invention also relates to a method of measuring the viscosity and/or density and other rheological properties of fluids.

**Background of Invention**

Atomic force microscopes (AFM) have been known since the mid 1980s. The AFM scans over the surface of a sample. Typically, in the "contact mode" of operation, a sharp tip is mounted on the end of a cantilever and the tip rides on the surface of a sample with an extremely light tracking force, of the order of $10^{-10}$ N. Profiles of the surface topography are obtained with extremely high resolution. Images showing the position of individual atoms are routinely obtained. In a second mode of operation, the tip is held a short distance, of the order of 5 to 500 Angstroms, from the surface of a sample and the tip is deflected by various forces between the sample and the tip; such forces include electrostatic, magnetic, and van der Waals forces.

Atomic force microscopy is capable of imaging conductive as well as insulating surfaces with atomic resolution. Typical AFM's have a sensitivity of 0.1 Angstrom in the measurement of displacement. The cantilever must be mounted so that the cantilever can approach and contact a sample.

Several methods of detecting the deflection of the cantilever are available which have Ångstrom or sub-Ångstrom sensitivity, including vacuum tunnelling, optical interferometry, optical beam deflection, capacitive techniques, magnetic, phase lock and piezoresistive measurements.

Micromachined and microfabricated cantilevers have subsequently been proposed for a range of applications including sensors for gas detection, bioassays, temperature, catalysis and magnetic field detection.

US patent 5,442,963 describes microsensors for measuring pressure. It

operates by calibrating the response against a series of calibration fluids. This prior art apparatus requires new calibration if there is a temperature change. It is also not applicable to measurements in small quantities of fluids.

As mentioned above, since the invention of the atomic force microscope (AFM), there has been extensive exploration of the force measurement and sensor applications of the instrument. In the latter class, AFM microcantilevers have been used as sensors for gas detention, mass measurement, temperature measurement, spectroscopy, and calorimetry.

One application that has received attention recently is the use of AFM microcantilevers in rheological measurements on liquids. By measuring the frequency response of a microcantilever immersed in a liquid, information regarding the rheological properties of the liquid, in principle, can be determined. However, this application is predicated on the frequency response of the microcantilever being sensitive to the rheological properties of the liquid under consideration. It is well known that the frequency responses of cantilevers of macroscopic size, say one meter in length, are sensitive to the viscosities of the fluids in which they are immersed. In contrast, for AFM microcantilevers, which are approximately 100 • m in length, liquid viscosity can significantly affect their frequency response. This property has permitted the use of microcantilevers as small-scale viscometers. However, this previous rheological application of microcantilevers is restricted to the measurement of liquid viscosity only, with density and the properties of gases being outside the realm of its applicability. In addition, a priori and independent measurement or knowledge of the liquid density is required, which in turn further restricts the utility of the microcantilever technique.

It would be desirable to have a microcantilever rheometer, as such analytical equipment would have many potential benefits over conventional methods such as vane and Couette rheometry. Such conventional viscometry equipment can be applied to homogeneous liquids only, over a limited range of viscosities and shear rate. However, in practice, these techniques are time consuming and require relatively large sample volumes. For biological fluids or for samples that need to be

analysed on-line, a technique capable of rapid measurements with small samples is desirable.

**Summary of the Invention**

This invention provides in one form a method of determining the viscosity and density and optionally other rheological properties of gases and liquids, by inserting a microcantilever rheometer into a sample of the fluid, measuring the cantilever frequency response and from this determining the viscosity and density and other optional rheological properties of the fluid, wherein the microcantilever rheometer has a single microcantilever.

Preferably the microcantilever rheometer comprises at least two microcantilevers that have different frequency responses.

Preferably the microcantilever is a rectangular cantilever.

In an alternative form the invention provides a microscale rheometer comprising at least one microcantilever, means to determine the frequency response, and means to calculate the density, viscosity and other rheological properties of a fluid to be tested.

In a further form the invention provides the use of the thermal noise frequency spectrum of a microcantilever to determine the density and viscosity and other rheological properties of a fluid.

Preferably the cantilever motion is detected through a piezoresistive device, and the cantilever itself is capable of being driven by a piezoelectric device.

Alternatively the cantilever motion is detected optically through a split

photodiode. Yet another method is to use the cantilever as one plate of a capacitor, and to measure the cantilever motion through the changes in capacitance.

In yet a further embodiment it is proposed that the cantilever have a magnetic coating. The cantilever may be driven in an arbitrary fashion using a magnetic coil. Likewise the coil could be used to monitor the cantilever motion.

Preferably a microcantilever is used to measure the rheological properties of fluids at very high oscillatory shear rates. These shear rates can be adjusted by modifying the microcantilever geometric and material properties.

The fast response times of microcantilevers enable real time monitoring of both density and viscosity and other rheological properties. Response times can be controlled by modifying the dimensions and material properties of the microcantilevers, and through modified detection systems and can be smaller than 1 μs. Knowledge of the temperature dependence of the material properties of the microcantilevers will also enable thermal rheometry to be performed.

**Description of the Drawings**

Figure 1: Shows a plot of relative viscosity vs volume fraction for a nanoparticle silica dispersion. Solid line is fit to Dougherty-Krieger formula.

**Detailed Description of the Invention**

In a preferred form microcantilevers with rectangular geometries are used for the simultaneous measurement of fluid (gas or liquid) viscosity, density and general rheological properties from the measurement of the cantilever frequency response. The fluids that are suitable for the present invention include gases and liquids. The range of fluid viscosities is very wide from $10^{-6}$ kg $m^{-1}s^{-1}$ to over 1 kg $m^{-1}$ $s^{-1}$. This range can be adjusted by varying the geometry and material properties of the microcantilever. The technique is applicable to both Newtonian and general non-Newtonian fluids. Indeed, it may be applied to a range of complex fluids such as dispersions, emulsions, polymers, gels and non-Newtonian fluids alike. A particular advantage of the present invention is that a single cantilever may be employed to measure the rheological properties of both gases and liquids. Due to its applicability to both gases and liquids, this technique can also be used to accurately monitor fluid

phase transitions and their properties, such as changes in density and viscosity and elastic properties. The fluid may be a supercritical fluid such as supercritical carbon dioxide, and superconducting fluids such as liquid Helium; a biological fluid, i.e. a fluid of biological origin, such as protein, blood, DNA, serum, saliva but also including other treated biological samples after dilution or stabilisation with buffers or reagents; a biofluid which may be agglomerating, agglutinating, gelling or precipitating either of its own accord, or as a result of an induced reaction with an added reagent; gel, emulsion, oil, petroleum product or crude oil, microemulsion, cosmetic composition with mixture of oils, colourants, fragrances; a food product or food ingredient.

Apart from these applications other uses are in the areas of hematology, biochemistry, immunology, microbiology, DNA assays, high throughput screening and the analytical detection of solutes.

Calibration prior to measurement is carried out in air with each cantilever, so no a priori assumptions about individual cantilever properties are necessary.

In an example of a preferred embodiment pure silicon, rectangular cantilevers of known geometry and spring constant were used. These were obtained from Park Instruments, and have no imaging tips. Their resonance frequencies correspond closely to the values predicted from the bulk material properties of silicon. The frequency responses of the cantilevers were measured by monitoring the cantilevers' Brownian motion, i.e., the thermal noise spectrum. This was performed in an atomic force microscope (AFM). The thermal noise spectra were collected using a National Instruments data acquisition card operating at 1.6MHz, and the resulting signal fast Fourier transformed using Labview software. The data were filtered using a Hanning function, then signal averaged to yield the final data. To avoid aliasing peaks, a number of digitising frequencies were used. The fundamental modes of the measured spectra were then fitted to the response of a simple harmonic oscillator (SHO) using a non-linear least squares fit. A white noise floor was also included to ensure accurate fits.

Measurements of gas properties were made in the fluid cell of the AFM, which consists of a white silicone rubber O-ring as cell wall and lucite cell roof and silicon wafer base. Gas of purity >99% was bubbled through the cell and then into a water solution which prevented diffusion of air back into the cell, and this solution also functioned as a gas flow indicator. Typically the flow rate was maintained at about 200$\mu$L/s. There was no discernible effect of flow rate on the data, except for hydrogen and helium, which will be discussed below. Cell temperature was maintained at 27 ± 0.5°C.

In Journal of Applied Physics, Vol 87, 3978-3988 (2000) ((J.W.M. Chon, P. Mulvaney, J.E. Sader), it was shown that for quality factors, Q > 1, the frequency spectra of rectangular beams could be fitted to the equation of a simple harmonic oscillator (SHO). This equation describes the response in terms of just two parameters, a resonance frequency and a single damping parameter, Q. To calibrate the cantilever, the cantilever's frequency response is measured in a fluid or gas of known viscosity and density, which will normally be air. The fundamental resonant peak is then fitted to eq.1, using $B$, $\omega_{R,n}$, $Q_n$ as fitting parameters.

$$A(\omega) = \frac{B(\omega)^2_{R,n}}{\sqrt{(\omega^2 - \omega^2_{R,n})^2 + \frac{\omega^2 \omega^2_{R,n}}{Q^2_n}}} \qquad (1)$$

Then from eqs.2 and 3 the two cantilevers calibration parameters can be determined, which are the cantilever's vacuum resonance frequency, $\omega_{vac}$, and the mass per unit length of the cantilever beam, $\mu$.

$$Q_n = \frac{\frac{4\mu}{\pi\rho b^2} + \Gamma_r(\omega_{R,n})}{\Gamma_i(\omega_{R,n})} \qquad (2)$$

$$\frac{\omega_{R,n}}{\omega_{vac}} = [1 + \frac{\pi \rho b^2}{4\mu} \Gamma_r(\omega_{R,n})]^{-1/2} \qquad (3)$$

Here, b is the cantilever width and $\Gamma$ is a complex hydrodynamic function, whose values are detailed elsewhere in Journal of Applied Physics (J.E. Sader), Vol. 84, 64-76 (1998). The beam may be constructed of any material or composite required, since the material characteristics enter only through $\mu$ and $\omega_{vac}$.

To measure the density and viscosity of an unknown fluid, the reverse procedure is then adopted. Here, the fundamental resonant frequency $\omega_{R,n}$ and quality factor $Q_n$ are measured, by fitting Eq.1 to the measured frequency response (fundamental resonance peak only, although higher harmonics may be used). Then the viscosity and density are calculated by solving Eqs.2 and 3 simultaneously. This process uses the numerical values for the cantilever's vacuum resonant frequency and mass per unit length as measured above in the calibration procedure.

Measured and literature values of $\eta$ and $\rho$, obtained from four liquids ranging in viscosity and density using two different rectangular Si microcantilevers of lengths 397 and 197$\mu$m are given in Tables 1 and 2 respectively. Typically the thermal noise frequency spectrum is obtained using more than 100 averages, with at least 16,384 points per spectrum. However, results within 1% of the values quoted here could readily be obtained with < 100 averages, which requires less than 30 seconds to accumulate. However with faster data acquisition, faster measurements are readily achieved. We stress that this averaging refers to thermal noise data only. Spectra were also collected after "ageing" the solution for 12 hours in the AFM to determine whether the data were susceptible to electronic or thermal effects within the photodiode and collection electronics. Identical data were obtained after 24 hours, provided the fluid temperature was maintained constant.

**Table 1**

| Fluid | Actual $\eta$ (kg m$^{-1}$ s$^{-1}$) | Values $\rho$ (kg m$^{-3}$) | Measured $\eta$ (kg m$^{-1}$ s$^{-1}$) | Values $\rho$ (kg m$^{-3}$) |
|---|---|---|---|---|
| Acetone | $3.03 \times 10^{-4}$ | 785 | $3.2 \times 10^{-4}$ | 754 |
| $CCl_4$ | $8.79 \times 10^{-4}$ | 1590 | $9.9 \times 10^{-4}$ | 1454 |
| Water | $8.59 \times 10^{-4}$ | 997 | $8.6 \times 10^{-4}$ | 968 |
| 1-butanol | $2.47 \times 10^{-3}$ | 805 | $2.8 \times 10^{-3}$ | 803 |

The liquid rheological properties fitted very well to eqs. 1-3. However, the cumulative errors in converting the frequency and Q into density and viscosity values was significant. The peak frequencies were easily monitored to within 10 Hz, i.e. < 0.1%, while Q is more complex, with values Q >>1 being accurate to about 1 – 2%, but for fluids of greater viscosity, the error rises to about 4 – 5%. Overall, errors ranging from about 1 – 14% for density and viscosity were obtained. Generally, lower viscosity media give better results since the higher Q resulted in more accurate fits. Nonetheless, the accuracy of these measurements can be improved by improving the theoretical model. Consequently, the errors mentioned should be considered as upper bounds.

To cover a broader range of density and viscosity values, and to demonstrate the applicability of a single microcantilever rheometer to both gases and liquids, we measured the density and viscosity of a variety of gases injected into the fluid cell using the same 397$\mu$m microcantilever as used to measure the liquid properties.

The substantially lower cantilever frequencies observed in liquids are due primarily to the much higher densities of liquids compared to gases. The increased viscosities contribute relatively less to the shift in frequency from vacuum. Gases have substantially lower densities than liquids, but also a broad range of values, with the resonance frequencies of cantilevers being very close to the vacuum frequencies.

The observed and literature values of the density and viscosity of gases are summarised in Table 3 using the 397 $\mu$m rectangular Si cantilever. The size of the

microcantilever can be varied. The results using a 97 $\mu$m rectangular Si cantilever are set out in Table 4.

**Table 2**

| Fluid | Actual Values $\eta$ (kg m$^{-1}$ s$^{-1}$) | Actual Values $\rho$ (kg m$^{-3}$) | Measured Values $\eta$ (kg m$^{-1}$ s$^{-1}$) | Measured Values $\rho$ (kg m$^{-3}$) |
|---|---|---|---|---|
| Acetone | $3.03 \times 10^{-4}$ | 785 | $3.2 \times 10^{-4}$ | 688 |
| $CCl_4$ | $8.79 \times 10^{-4}$ | 1590 | $8.4 \times 10^{-4}$ | 1397 |
| Water | $8.59 \times 10^{-4}$ | 997 | $7.4 \times 10^{-4}$ | 890 |
| 1-butanol | $2.47 \times 10^{-3}$ | 805 | $2.49 \times 10^{-3}$ | 694 |

For most of the gases, strong distinctive shifts in spectra were noted as the new gas was pumped through the cell, and data could be collected within a minute or two of purging. All the gases gave reproducible spectra over time, provided there was a steady gas flow through the AFM cell. When the gas flow was stopped, the spectra began to change. This effect was most pronounced for the "lighter" gases, helium and hydrogen. This indicated the diffusion of gas out of the cell through the porous O – ring. The half-life for the spectrum to return to its air values was about 3 – 4 minutes.

To demonstrate the feasibility of using microcantilevers to measure the rheological properties of complex fluids, in Fig. 1 we present measurements of the viscosity of a silica nanoparticle dispersion (40 nm diameter silica nanoparticles dispersed in water) as a function of volume fraction. It is observed that the viscosity of the dispersion increases with increasing volume fraction Ø, as expected. Further, the result of a fit to the Dougherty-Krieger formula is also shown. This gives the following expression for the relative viscosity of the dispersion as a function of volume fraction Ø:

$$\frac{\eta_{dispersion}}{\eta_{water}} = \left(1 - \frac{\phi}{0.214}\right)^{-0.539} \qquad (4)$$

Eq. (4) predicts that the dispersion will gel at a volume fraction of 21.4%. This value is well below the hard sphere limit, and is consistent with the presence of interparticle forces between the silica nanoparticles. Interestingly, by formally expanding eq. (4) for small volume fractions we obtain

$$\frac{\eta_{dispersion}}{\eta_{water}} = 1 + 2.5\phi + 9.0\phi^2 \qquad (5)$$

The coefficient 2.5 multiplying the linear term in Ø is exactly as expected from theoretical considerations and is independent of any interparticle forces. In contrast, the quadratic term is known to depend strongly on the interparticle forces. In the hard sphere limit, the coefficient multiplying the quadratic term in Ø is predicted to be 6.2. Here we find a larger value of 9.0, which is consistent with the presence of interparticle forces. These results illustrate the feasibility of using microcantilevers to perform detailed rheometry on colloidal dispersions.

**Table 3**

| Fluid | Actual $\eta$ (kg m$^{-1}$ s$^{-1}$) | Values ρ (kg m$^{-3}$) | Measured $\eta$ (kg m$^{-1}$ s$^{-1}$) | Values ρ (kg m$^{-3}$) |
|---|---|---|---|---|
| Air | $1.86 \times 10^{-5}$ | 1.18 | $1.87 \times 10^{-5}$ | 1.16 |
| Helium | $2.0 \times 10^{-5}$ | 0.164 | $2.2 \times 10^{-5}$ | 0.14 |
| Carbon dioxide | $1.5 \times 10^{-5}$ | 1.817 | $1.54 \times 10^{-5}$ | 1.73 |
| Nitrogen | $1.79 \times 10^{-5}$ | 1.23 | | |
| Hydrogen | $8.8 \times 10^{-6}$ | 0.083 | $8.97 \times 10^{-6}$ | 0.11 |
| Argon | $2.33 \times 10^{-5}$ | 1.61 | $2.39 \times 10^{-5}$ | 1.48 |

**Table 4**

| Fluid | Actual Values | | Measured Values | |
|---|---|---|---|---|
| | $\eta$ (kg m$^{-1}$ s$^{-1}$) | $\rho$ (kg m$^{-3}$) | $\eta$ (kg m$^{-1}$ s$^{-1}$) | $\rho$ (kg m$^{-3}$) |
| Air | $1.86 \times 10^{-5}$ | 1.18 | $1.69 \times 10^{-5}$ | 1.20 |
| Helium | $2.0 \times 10^{-5}$ | 0.16 | $2.2 \times 10^{-5}$ | 0.14 |
| Carbon dioxide | $1.5 \times 10^{-5}$ | 1.81 | $1.5 \times 10^{-5}$ | 1.69 |
| Nitrogen | $1.79 \times 10^{-5}$ | 1.23 | $1.5 \times 10^{-5}$ | 1.2 |
| Hydrogen | $8.8 \times 10^{-6}$ | 0.083 | $9.0 \times 10^{-6}$ | 0.11 |
| Argon | $2.33 \times 10^{-5}$ | 1.61 | $2.0 \times 10^{-5}$ | 1.54 |

The above data clearly demonstrate that a single microcantilever can act as a direct nanosensor of the density and viscosity of gases, liquids and complex fluids. Both parameters are important and inseparable. For unknown fluids, rheological data can only be measured from fits to both variables.

The method of the present invention is rigorous and measures density and viscosity a priori, whereas other methods rely on calibration fluids and some arbitrary interpolation function. These other methods are sensitive to the temperature of measurement since the viscosity of the calibration fluids will change at different temperatures. Conversely, the stiffness of the microcantilever itself is basically independent of temperature.

The method is extremely useful for biological fluids because calibration fluids would contaminate the sensor.

The cantilever in one embodiment may be purpose-built into, and integrated within, a microfluid cell as a complete flow-through device and sensor.

The cantilever may itself be further modified to fulfil other roles. e.g. it may be a composite lever, it may have layers on it to make it compatible with the solvent or gas, and it may have other sensor functions. These auxiliary properties do not

change its role as a viscosity and or density sensor. In particular in biological assays it may have biological surface components.

The method can be used to monitor phase transitions .e.g. gases to liquids, liquids to solids, liquids to gels, gels to solids, gases to solids, (as well as supercritical $CO_2$, or superfluids like He, mentioned already.)

Provided the cantilever oscillations are small in magnitude, such as when excited by thermal fluctuations, the technique does not perturb the medium. Other techniques that require large amplitude oscillations can shear the medium significantly.

The method can be used to detect filling and emptying of channels both nanoscopically or macroscopically e.g. in microfluid cells, in petrol tanks, or in any closed volume where on-line fluid level monitoring may be advantageous. Other uses include detecting leakages, sensing the mixing of fluids and measurements of humidity.

The method outlined above can be applied to more complex fluids, e.g., where the viscosity may become time dependent, such as in shear thinning/thickening fluids, or in fluids undergoing a gelling process (as demonstrated above), or in fluids exhibiting general viscoelastic behaviour where general rheological properties can be probed.

The cantilever can probe fluid volumes less than 1 nanolitre, making it thousands of times more "efficient" than any other technique and opens up the possibility of performed spatially resolved rheological measurements.

One limitation with using the conventional AFM detection system described above, is that the optical detection method employed here precludes direct measurement of opalescent or turbid media, since even slight light scattering drastically reduces S/N ratios. However, this may be avoided by use of piezoresistive detection or other detection systems that are not restricted by the optical properties of the medium. This includes common methods of cantilever motion detection such as capacitive, quantum tunnelling, magnetic or combinations of these. Likewise, signal to noise can be improved by employment of magnetically

driven or piezoelectric cantilevers or other means of directly exciting the microcantilevers. However, it is an important advantage of the microcantilever rheometer that it can function using only thermally excited cantilever motion, which constitutes the minimum possible perturbation by a lever of the medium.

Microcantilever rheometry offers the potential characterisation of microscopic liquid drops, and minute gas samples. For example, in " DNA chips" and other microfluid based analytical methods, sub-microlitre quantities of biological fluids flow through channels for separation and analysis. Flow in the confines of such devices may be impeded by even slight gelation, or channel blockage or aggregation of fluids due to polymerisation or crosslinking. Microcantilevers may be used to monitor the fluid character during flow in a non-intrusive and non-invasive manner. It is feasible for direct in vivo measurement of blood viscosity by insertion of a needle with microcantilever probes.

The invention also opens up the possibility of performing high frequency rheological measurements for the first time. Current instrumentation is limited to frequencies less than 10-100 Hz. In contrast, a microcantilever can probe frequencies anywhere from 100 Hz to 10 MHz or greater. The range of frequencies accessible is dictated only by the geometry and material properties of the cantilevers. These parameters, especially the geometry can be easily controlled and modified. Deviations from Newtonian flow can consequently be discerned from the frequency spectrum.

Claims

1. A method of determining the viscosity and density and optionally other rheological properties of gases and liquids by inserting a microcantilever rheometer into a sample of the fluid, measuring the cantilever frequency response and calculating the viscosity and density and other optional rheological properties of the fluid wherein the microcantilever rheometer has a single microcantilever.

2. A method as defined in claim 1 wherein the microcantilever rheometer comprises a further microcantilever that has a different frequency response to the other microcantilever.

3. A method as defined in any one of claims 1 to 2 wherein the microcantilever is a rectangular cantilever.

4. A method as defined in any one of claims 1 to 3 wherein the cantilever motion is detected through a piezoresistive device, and the cantilever itself is capable of being driven by a piezoelectric device.

5. A method as defined in any one of claims 1 to 3 wherein the cantilever motion is detected by non-optical means.

6. A method as defined in any one of claims 1 to 3 wherein the cantilever motion is excited actively.

7. A method as defined in any one of claims 1 to 3 wherein the cantilever motion is excited passively through thermal fluctuations.

8. A method as defined in any one of claims 1 to 3 wherein the cantilever is one plate of a capacitor, and the cantilever motion is measured through the changes in capacitance.

9. A method as defined in any one of claims 1 to 8 wherein oscillating shear rates are greater than 100 Hz.

10. A microscale rheometer comprising at least one microcantilever, means to determine the frequency response, and means to calculate the density and viscosity and optionally other rheological properties of a liquid or gas to be tested.

11. A method for monitoring the changes in viscosity and density or elastic properties of a volume of fluid less than a millilitre as a function of time using a

microcantilever rheometer.

12. A method for monitoring the rheological properties of a fluid using a microcantilever rheometer wherein the cantilever is constructed from a single material.

13. A method for monitoring the rheological properties of a fluid as defined in claim 12 wherein the cantilever is constructed from a composite material.

14. A method for in vivo monitoring of biological fluids such as blood or saliva or gases inhaled into lungs using a microcantilever rheometer.