

# Viscosity measurements of PEO solutions by AFM with long nanowires

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## ABSTRACT

Long, constant diameter nanowires on the end of atomic force microscope (AFM) probes are expected to provide clean force distance (F-D) measurements that are easily interpretable. For measurements of the viscosity of low molecular weight liquids this proves to be true. Comparable values are found for glycerol when the nanowire is drawn from the liquid at a constant velocity over microns in scan length and when the nanowire insertion depth changes no more than that due to thermal Brownian vibration fluctuations, as is used for the  $Q$  damping measurement method — which also matches macroscopic viscometry methods. However, for measurements of the high molecular weight random chain polymer poly(ethylene oxide) (PEO) the differences are dramatic, with the  $Q$  damping method giving values that are orders of magnitude smaller than the linear drag force measurement. Since the deflection amplitude is sub-nanometer, the unusually low viscosity might be due to displacements that are smaller than the entanglement length of the polymer. Additional preliminary investigations are reported that do show somewhat increased viscosity with 10X increased vibration amplitude. Also time dependence of the measurements appears to be related to adsorption of monolayer coatings of PEO on the needle.

**Keywords:** AFM, viscosity, drag force,  $Q$  damping

## 1 INTRODUCTION

With increasing practical applications of microfluidics, lab-on-a-chip, and micro-reactors, it is becoming increasingly important to develop *in situ* nanoscale sensors of fluid mechanical properties; *e.g.* surface tension, contact angle, evaporation rate, viscosity. Principles and methods from atomic force microscopy, with suitably designed probes, can be adapted to sense such properties in small confined environments or with miniscule quantities of sample. For the measurement of viscosity, a long, constant diameter probe tip is highly desirable because drag force is proportional to insertion depth, which enables values of drag force to be produced that are in the detectable range of the AFM detection circuitry. Additionally, the constant diameter means that the wetting force due to surface tension is constant with insertion depth (due to the constant length of the contact line). With standard tapered AFM probe tips the wetting force (as well as the change in drag force) changes dramatically with insertion depth.

A few groups have reported on the use of (custom formed) constant diameter probe tips to measure surface tension [1]. Mechler *et al.* [2] have utilized the lateral force mode (friction mode) of the AFM to scan carbon-nanotube tipped probes in glycerol/water films. Torsional bending of the cantilever is then related to the drag force. The force-distance (F-D) mode, where the probe is scanned perpendicular to the surface and the force is determined from the bending of cantilever, also provides a direct and general method to measure liquid forces [3].

For the determination of viscosity we use a ten's of microns long, constant diameter metallic nanowire (or "nanoneedle") on the AFM probes to measure drag force (Fig. 1). The needle is custom grown on the cantilever by a room temperature process [4]. Drag force is then measured by drawing the needle with a known velocity and at a known insertion depth from the liquid while recording the F-D response. Viscosity is then determined from the well-known expression for longitudinal drag on a cylindrical object.

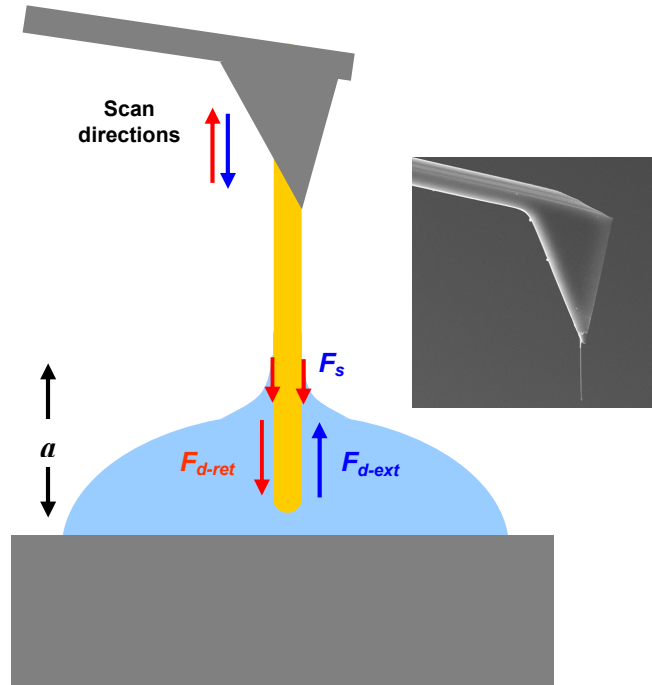


Figure 1. Viscosity measurement setup with nanoneedle-tipped probes. The inset is an SEM image of a needle-tipped probe. Forces considered in the measurements are shown for retraction (red) and extension (blue) scans.

Drag force on a needle, and thereby viscosity, also can be related to the damping it produces on an attached mechanical resonator. The AFM cantilevers generally do have high  $Q$  and the AFM detection circuitry is sensitive enough to measure damping changes in the amplitude vibration spectrum of the cantilever due to thermal (Brownian) fluctuations in the cantilever position. These features are part of the standard AFM sensing mode referred to as the  $Q$  damping method.

These two measurement methods are found to give the same results for low molecular weight liquids, in correspondence with macroscopic viscometry measurements. However, for highly viscous solutions containing the random chain polymer PEO, we find that the  $Q$  damping method under-reports viscosity by orders of magnitude. This paper reports on our initial measurements of both low molecular weight glycerol/water solutions and of aqueous PEO solutions, as well as experimental evaluation of some factors that affect the values of viscosity in the  $Q$  damping method. It will be quite interesting and physically informative if the  $Q$  damping method turns out to provide detailed information on interactions between polymer chains at molecular length scales that are smaller than the length of the polymer chains.

## 2 MEASUREMENT PRINCIPLES AND EXPERIMENTAL METHODS

Figure 1 shows the experimental setup, which is identical for both the  $Q$  damping method and the constant velocity/linear drag force method.

### 2.1 Viscosity from constant velocity scans

The AFM is configured to produce F-D scans of retraction and extension as the needle is translated normal to the surface of the liquid. Drag force  $F_d$  sensed by the cantilever deflection is oppositely directed from the scan motion, while surface tension induced force  $F_S$  is directed downwards (for contact angle less than  $90^\circ$ , which was the case for all liquids studied.) The total force,  $F_T$  applied to the needle during the retraction is

$$F_T = -(F_S + F_{d-ret}) \quad (1)$$

where  $F_{d-ret}$  is the drag force during the retraction. For long cylindrical needles the drag force in the axial direction of the needle is [5]

$$F_d = \frac{4\pi\eta a v}{\ln(2a/r) - 0.81} \quad r \ll a \quad (2)$$

where  $a$  is the submerged length of the needle,  $r$  is the radius of the needle and  $v$  is the scan speed. The surface tension force applied to the needle is

$$F_S = 2\pi r \sigma \cos(\theta) \quad (3)$$

where  $\sigma$  is the surface tension and  $\theta$  is the contact angle of the liquid surface. The F-D curve records the total force applied to the cantilever at any immersion depth of the needle. When the needle breaks free of the liquid, a stepwise change in the force curve equal to  $F_S$  occurs [1]. This step in the force curve locates the reference height of the liquid, thereby providing the immersion depth of the needle throughout the scan. The viscosity is determined by repeating the experiment at different scan velocities. The slope of a graph of drag force at a constant insertion depth gives the viscosity of the liquid.

### 2.2 Viscosity from $Q$ damping

The  $Q$  damping mode is a standard feature of the Asylum MFP3D AFM used in this study. Mechanical excitation is normally produced by Brownian thermal fluctuations. In some experiments we introduced an electrically generated white noise to the cantilever holder's piezoelectric shaker, to produce somewhat larger amplitude fluctuations. When a needle is partially inserted into a liquid (Fig. 1), the  $Q$  of the resonator is reduced to

$$Q = \frac{\sqrt{Mk_c}}{R} \quad (4)$$

where  $M$  is the effective mass of the cantilever,  $k_c$  is the cantilever spring constant and  $R$  is the drag coefficient. (Note that damping due to the liquid generally reduces the  $Q$  substantially, thereby eliminating the consideration of air, and other sources of damping on the cantilever.) The drag coefficient in the axial direction of the needle is calculated by equation (2). From equations (2) and (4),  $Q$  can be related to viscosity  $\eta$  as

$$\frac{1}{Q} = \frac{1}{\sqrt{Mk_c}} \frac{4\pi\eta a}{[\ln(2a/r) - 0.81]} \quad (5)$$

The value of  $M$  is established by using a reference liquid of known viscosity. Typically we use water which is 1 cP at  $20^\circ\text{C}$ . Then the value of  $\eta$  is the only unknown parameter in equation (5). The needle is especially convenient in that equation (5) can be fit for several values of the insertion depth  $a$ , which can be used to average out measurement errors.

Cantilever characteristics [6] and the characteristics of the attached nanoneedles [7a-e], are described in the references.

## 3 EXPERIMENTAL MEASUREMENTS

### 3.1 PEO viscosity by constant speed scans

The method from Sec. 2.1 is used together with equations (1) and (2) to evaluate the viscosity of a 4 wt % PEO

(1,000,000 MW) aqueous solution. The needle [7a] is inserted a few microns into the liquid and retracted from the liquid at a constant velocity while recording the F-D curve is recorded. Figure 2 shows the total force  $F_T$  for retraction speeds from 12 to 98  $\mu\text{m/s}$  at a 2  $\mu\text{m}$  insertion depth. The slope of the linear fit corresponds to a viscosity of 2,200 cP. A larger sample of the same liquid sample is measured to be 2,342 cP in a Brookfield LV-DV II+ cone and plate viscometer. In the AFM measurements the laboratory temperature varied between 21 and 24  $^\circ\text{C}$  and in the cone-plate viscometer the laboratory temperature varied between 21 and 23  $^\circ\text{C}$ .

Additionally, the linear fit gives a wetting force  $F_S = 62.74$  nN at zero scan velocity. The surface tension of 3 wt % PEO and higher has been reported to be 62.6 mN/m. [8] From equation (3), the receding contact angle is calculated to be 48.3  $^\circ$ .

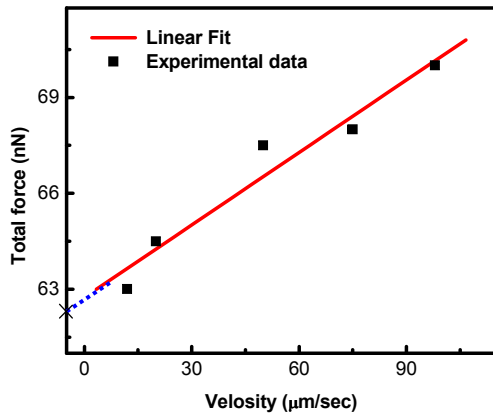


Figure 2. Measurement of total force and its resolution into drag force and wetting forces for 4 wt % PEO.

### 3.2 Glycerol and PEO by $Q$ damping

First a series of glycerol/water solutions were measured from 0 to 100 wt % glycerol. The needle is inserted to several depths  $a$  into the liquid, and  $Q$  is recorded for each depth. The data is fit to equation (5) as a function of the unknown value of viscosity. The insertion depths used are 1.5  $\mu\text{m}$  or greater which ensures that the needle is a long slender cylinder, as is assumed by the model drag force in equations (2) and (4). As described above, the published value for water (0 wt % glycerol) is used as a reference value to establish the value of effective mass  $M=1.3 \times 10^{-9}$  gm used in equation (5) for the needle-tipped cantilever used [7b]. Fits to three of these solutions are shown in Fig. 3a and the determined viscosity is plotted in Fig. 3b, along with all the measured viscosities. We also measured and graphed the identical solutions for cone-and-plate viscometer measurements (at shear rates from 1350/s for pure water down to 1.5/s for pure glycerol). The plots also show published viscosity values [9]. The viscometer data and AFM data generally track each other, as well as the general trends in the published data at 20 and 30  $^\circ\text{C}$ . The

published data does make evident the need to regulate the temperature for highly accurate measurements.

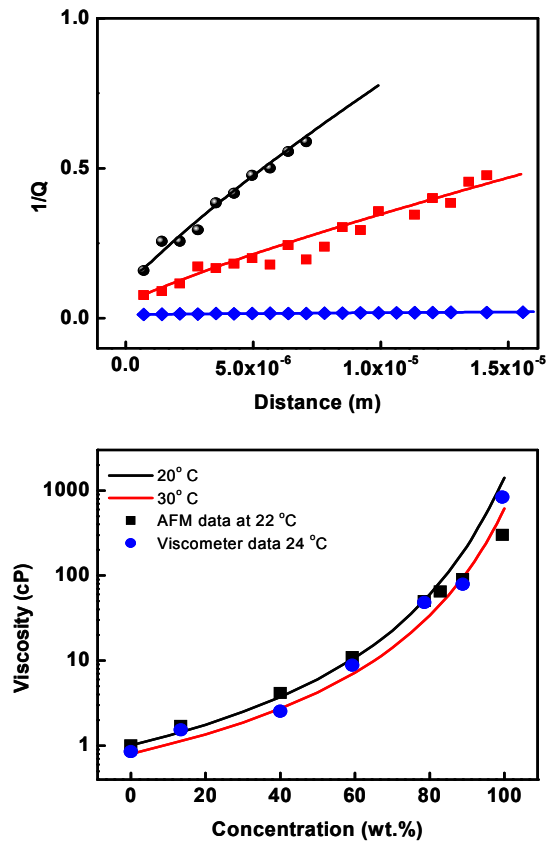


Figure 3. Thermal  $Q$  damping measurements of solutions of aqueous glycerol. (a) Reciprocal of  $Q$  as a function of insertion distance. Experimental data and best fit curves to equation (5) for 13.5, 80 and 99.5 wt % glycerol (from lowest to highest curve). (b) Values of viscosity from best fits of equation (5) to data sets of the type in (a). Plot also includes cone and plate viscometry measurements and published values [9]. The relative standard deviation for each measured data point varies from 4 % (for the highest concentration) to 20 % (for pure water).

PEO, especially of high molecular weight, is difficult to completely dissolve and mix in water. At 4 wt % and higher we observe that the solution becomes cloudy. At these concentrations the polymer can coat the needles [7c] to a noticeable degree, which can form a large blob or long string if the tip is not frequently rinsed clean in pure water. Solutions above 4 wt % proved to be too difficult to work with by the AFM method. These problems are not evident in the viscosity measurements using the cone-and-plate viscometer. The resulting AFM and viscometer measurements are compared in Fig. 4. The AFM measurements depart dramatically from the viscometer measurements with increasing concentration. The largest value of viscosity measured by AFM is only  $\sim 5$  cP for 4 wt % PEO, which is far lower than the viscosities measured for glycerol solutions in Fig. 3. The  $Q$  damping experiment was

repeated using a softer cantilever ( $k_c < 0.1$  N/m) in order to produce an increased thermal amplitude fluctuation. For PEO of 3 wt % the measured value for viscosity in Fig. 4 increases, but still is far below that for the cone and plate viscometer. This increase may be due to increase in the amplitude of the cantilever vibration. Because the cantilever is actuated by Brownian thermal fluctuations the cantilever displacement is sub-nanometer, which suggests the possibility that the cantilever does not fully engage the entanglements between the random chains of the PEO.

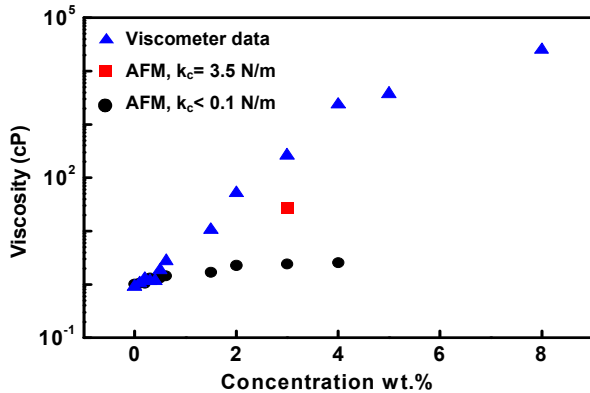


Figure 4. Viscosity measurements of PEO solutions.

In order to explore this we further actuated the cantilever by applying a white noise source to piezoelectric shaker, increasing the cantilever [7d] displacement by a factor of 10X. While this increase in amplitude showed no change in the measured viscosity of glycerin, in 2 wt % PEO it showed an increase from 2 cP to 4 cP. This can be seen in the increased slope of  $1/Q$  versus insertion depth of the needle into the liquid in Fig. 5a. The viscosity calculated from a macroscopic drag force equation is still smaller than the macroscopic viscosity by orders of magnitude. With the current AFM setup it is not possible to extend the cantilever oscillation amplitude further.

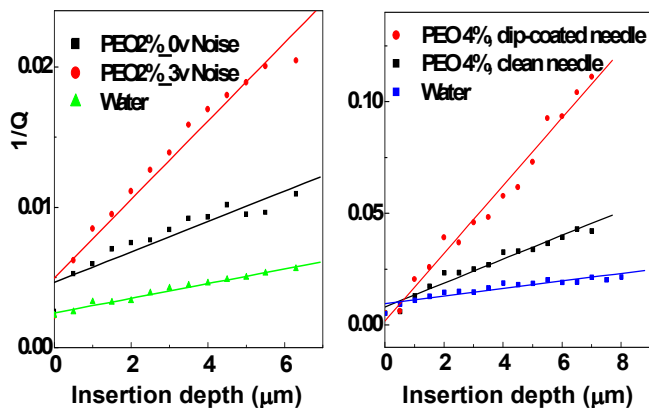


Figure 5.  $Q$  damping measurements of PEO solutions for various insertion depths. (a)  $Q$  damping by the application of white noise to a piezo shaker (red curve) is greater than with purely thermal actuation (black curve). (b)  $Q$  damping increases when the needle adsorbs PEO (red curve) compared to a freshly cleaned needle (black curve).

A second set of experiments with 4 wt % PEO shows that the viscosity changes from 3.1 cP when the needle [7e] is first immersed in the liquid, to 8.9 cP 10 minutes later. Since no coating is observable in SEM images, this suggests that only a few monolayers of PEO are adsorbed to the needle, which nonetheless influences the interaction of the needle with the liquid. Table 1 summarizes the results for various types of measurements on PEO.

Table 1. Viscosity of aqueous PEO by various methods

AFM Method	PEO (wt %)	Viscosity by AFM (cP)	Viscosity by viscometer (cP)
Q (thermal)	2	2	52
Q (electrical)	2	3.8	52
Q (fresh)	4	3.1	2,342
Q (10 min)	4	8.9	2,342
Linear drag	4	2,200	2,342

## 4 CONCLUSIONS

Probing polymeric solutions with nanoneedles has identified differences between the linear drag force and  $Q$  damping methods that raise the intriguing possibility of being able to measure continuous transitions between molecular scale and macroscopic viscosity.

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- [7] The probes are specialized with (a) a  $30 \mu\text{m}$  long  $\times$   $480$  nm diameter needle, (b) a  $20 \mu\text{m}$  long  $\times$   $362$  nm diameter parylene coated needle (including coating thickness), (c) a  $57.5 \mu\text{m}$  long  $\times$   $388$  nm diameter parylene coated needle, (d) a  $48.48 \mu\text{m}$  long  $\times$   $532$  nm diameter needle on a cantilever of  $350 \pm 15$  kHz resonance frequency and  $28.5 \pm 1$  N/m spring constant, (e)  $33.57 \mu\text{m}$  long  $\times$   $376$  nm diameter needle. The cantilever used for (e) has a spring constant of 25 N/m and is from Budget Sensors.
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