

ATOMIC FORCE MICROSCOPY CALIBRATION METHODS FOR LATERAL FORCE, ELASTICITY, AND VISCOSITY

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ABSTRACT

Due to huge uncertainties in the geometric dimensions of atomic force microscopy (AFM) probes, samples' rheological properties and lateral forces are difficult to measure and compare quantitatively. Hence, mathematical calibration methods fail to calibrate AFM probes accurately. To solve this problem, we will introduce in this paper "blind calibration methods" to determine quantitatively lateral forces, elastic constants and viscosity. For lateral force, a geometry factor is used to calibrate any cantilever using this "blind method". The essential part of this method is a calibration standard sample that is commercially available. We have chosen silicon for our calibration standard sample and will discuss a cleaning procedure for reproducible lateral force measurements. We will provide an absolute friction value, which will serve as one of three parameters necessary to obtain the geometry factor. The other two components being the normal spring constant and the relative friction signal measured with the cantilever of interest. Further, we will discuss force modulation measurements and the problems that occur around resonances. We will provide a procedure to determine elastic constants also based on the silicon calibration standard. Finally, the "blind calibration method" will also be used to achieve kinematic viscosity values.

INTRODUCTION

Over time, mechanical and viscous properties have been studied extensively for bulk materials. But what happens when these systems are reduced only to thin films and the interfacial effects start to interfere with the bulk properties? Due to the variety of technical applications of thin films, it is important to achieve an improved understanding about their surface and interfacial properties. Since the invention of the atomic force microscope (AFM) in 1986 by Binnig et al. [1], the AFM has become an increasingly important instrument for understanding surface properties. Using the AFM, many groups have studied polymer yield forces by lateral force measurement [2], elastic compliance of thin films [3] and liquid viscosity gradients [4]. However, measurements are still difficult to quantify due to uncertainties in the cantilever tip geometry and the complex deflections of the cantilever. As a result, mathematics and computer models fail to calculate AFM cantilever probes accurately or are too time consuming to be an effective calibration technique. Experimentalists need to have reliable time-effective calibration methods, which are easily reproducible in other laboratories with a minimum of instrumentation and computer efforts. In this paper, we introduce "blind" calibration methods for friction, elasticity, and kinematic viscosity. From the instrumental point of view only an AFM system and an oscilloscope are necessary for calibrating lateral forces if the normal spring constant is known. For elasticity and kinematic viscosity measurements, a function generator and lock-in amplifier are additional pieces of equipment needed. We use silicon as the calibration standard surface, which is available in most AFM laboratories.

EXPERIMENT

A commercial AFM (*Explorer* from Topometrix Inc.) which is based on a laser beam deflection detection scheme is used in this study in conjunction with a digital oscilloscope (54601B, Hewlett Packard), a dual phase lock-in amplifier (SR830, Stanford Research Systems), and a function generator (DS345, Stanford Research Systems). Cut silicon wafers (100) (Silicon Sense Inc.) are used as calibration standard samples. The silicon wafers are cleaned via sequential sonication in acetone (15 minutes) and methanol (30 minutes) (HPLC grade from commercial sources) then rinsed with ultra-pure water (MilliQ systems). In a low humidity environment, the silicon calibration standard surfaces are heated above 100°C to remove excess water. These samples provide reproducible values over a time period of two hours. Lateral forces are obtained through the oscilloscope as the calibration standard is scanned over 20 μm at 1Hz. All measurements are performed at a constant temperature using a sample heating/cooling system (R27002, MMR Technologies Inc.) in an environmental chamber under low humidity (<5 %). The binary system of polyethylene acrylate (PEA)/PEA grafted with polystyrene (PEA-g-PS) used for elasticity measurements are prepared by spin coating the polymers onto HF treated silicon substrates. The films are annealed and dried at 110 °C [5].

RESULTS AND DISCUSSION

Calibration of Friction

For known normal spring constants, the following “blind” calibration method is applied to quantify measured lateral forces, which occur during the scanning process. The normal spring constant of a cantilever is calibrated by measurement of the thermally activated power consumption [6] or by the addition of known masses (styrene spheres) [7] among other methods. The normal load which is the sum of the applied load and the adhesive load ($F_N = F_L + F_{adh}$) can be determined by:

$$\Delta F_N = k_N \frac{\Delta I_N}{S} \quad (1a)$$

$$k_N = \frac{EWT^3}{4L^3} \quad (1b)$$

where k_N is the normal spring constant, S is the sensitivity of the photodiode, ΔI_N is the signal from the detection scheme of the deflection of the cantilever in the normal direction, E is the Young's modulus and W , T , and L are the width, thickness, and length of the cantilever, respectively. Likewise, lateral force can be determined by:

$$\Delta F_T = \frac{3}{2} \frac{k_T R}{SL} \Delta I_T \quad (2a)$$

$$k_T = \frac{GWT^3}{3LR^2} \quad (2b)$$

where k_T is the torsional spring constant, R is the length of the cantilever tip, ΔI_T is the signal from the detection scheme of the torsional deflection of the cantilever, and G is the shear modulus.

From these equations, a well defined cantilever characterized by scanning electron microscopy (SEM) was found to have a friction coefficient on the silicon calibration standard sample (see above) of:

$$\mu_{Si-Si} = \frac{\Delta F_T}{\Delta F_N} = 0.18 \pm 0.03 \quad (3)$$

With this absolute friction coefficient on silicon, any cantilever of unknown torsional spring constant can be calibrated by:

$$\Gamma = \mu_{Si-Si} \left(\frac{\Delta I_T^{cal}}{\Delta F_N^{cal}} \right)^{-1} \quad (4)$$

where ΔI_T^{cal} is the torsional signal (in our case the lateral photodiode signal) measured with the unknown cantilever in sliding contact with the silicon calibration standard under a load of ΔF_N^{cal}

To find Γ , we first determine for the unknown cantilever the “qualitative” coefficient of friction, α , which is defined as the ratio between the horizontal (lateral) photodiode signal and the vertical (normal) photodiode signal; i.e.:

$$\alpha = \frac{\Delta I_T^{cal}}{\Delta I_N^{cal}} \quad (5)$$

This “qualitative” friction coefficient is missing any geometrical information about the unknown cantilever. Next, we introduce the normal spring constant and photodiode sensitivity to Eq. (5) to obtain a non-dimensionless friction coefficient, μ^* .

$$\mu^* = \frac{\alpha S}{k_N} \quad (6)$$

A “torsional geometry” factor can now be calculated by normalizing the non-dimensionless calibration friction coefficient by the absolute friction coefficient for silicon, $\mu_{Si-Si} = 0.18 \pm 0.03$.

$$\Gamma = \frac{\mu_{Si-Si}}{\mu^*} = \mu_{Si-Si} \left(\frac{\Delta I_T^{cal}}{\Delta F_N^{cal}} \right)^{-1} \quad (7)$$

Finally, without changing the laser position, the lateral force on any sample can be calculated for that particular cantilever by multiplying the relative friction signal, I_T , by the geometry factor; e.g.:

$$F_T = \Gamma I_T \quad (8)$$

The Effect of Contact Resonances on Force Modulation Measurements

In polymer rheology, it is well known that polymeric systems show a strong frequency dependence in their viscoelastic response, which is of great interest to be studied. Resonances, however, coming from the AFM should be avoided. At resonances there are no amplitudes defined. With the loss of knowledge about the amplitude, the force modulation method at any resonance of the system seems to be reduced to a mere qualitative stiffness measuring tool. Our measurements discussed below and studies from the Liu group show that at contact resonances an enhanced contact force modulation response map can be recorded between multicomponent systems [8]. Resonance measurements provide, therefore, only the information about the existence of heterogeneities in stiffness. They do not identify the stiffer (or softer) areas nor provide absolute or relative values, but merely provide the operator with an idea about variations in the rheological properties of the sample.

A sinusoidal modulation (A_{in}) is applied to the cantilever, and the response of the cantilever is measured (A_{out}). The cantilever response from a sample is then compared to the response from our calibration standard, silicon. We assume that the calibration sample is infinitely hard and that minimal damping occurs between the input and output responses. The

amplitude response of the cantilever while in contact is larger for a harder sample than a softer one. From contact mechanics, the Young's modulus can be determined within the elastic limit from a measure of the distance that the cantilever deforms the surface, δ .

Measurements of the response amplitude on a polyethylene acrylate (PEA)/PEA grafted with polystyrene (PEA-g-PS) show two different elastic responses for the sample at different frequencies, Fig. 1(a,b). The problem that we are faced with is to determine if the elastic responses in Fig. 1(a,b) are material-frequency dependent responses or an artifact due to system resonances.

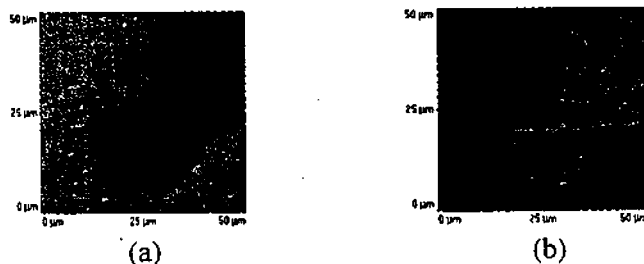


Figure 1(a,b). The PEA/PEA-g-PS system shows two different elastic responses for the sample at different frequencies. The lighter areas denote a presumably "stiffer" surface while the darker areas denote a presumably "softer" surface. (a) 3.65 kHz (b) 3.9 kHz

From the contact frequency spectrum on our infinitely stiff test sample, silicon, the amplitude of the cantilever response is found to be frequency dependent, Fig 2(a), which limits the results obtain in Fig 1(a,b) to an AFM system artifact. At nearly every point on the spectrum, the amplitude is strongly affected by resonances. Elimination of resonance sources, (e.g. acoustic noise sources, shielding of cables) reduces the number of resonances as shown in Fig 2(b). The flat areas are now those that are suitable for force modulation measurements. Measuring the response amplitude in the resonance free regimes of Fig. 2(b), we are able to determine that

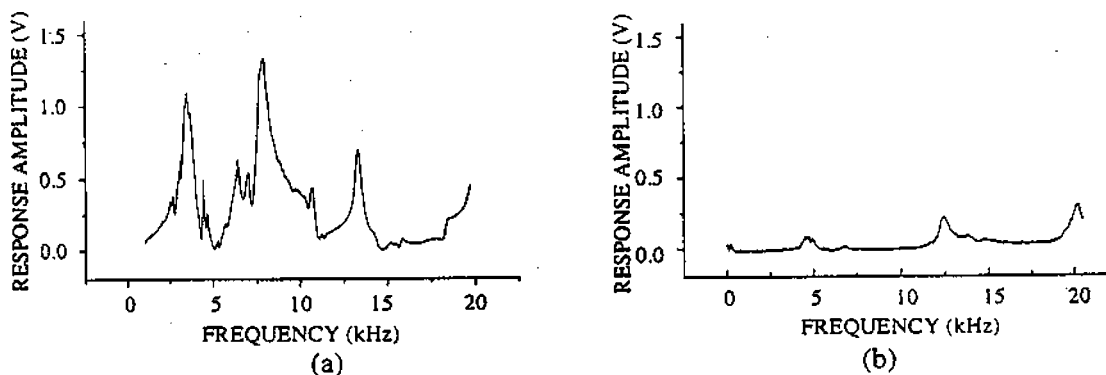


Figure 2(a,b). Contact frequency spectrums on silicon. (a) System before elimination of resonance sources (i.e. lighting, shielding of cables, et cetera). The response amplitude is assumed to be a function of frequency. (b) System after elimination of resonance sources. Flat regions are ideal areas to measure elastic response.

Fig. 1(b) is showing the correct elastic contrast confirmed by low frequency calibration measurements for the PEA/PEA-g-PS system [3]. These results are also consistent with friction measurements and glass temperature data.

Calibration of Viscosity Measurements

The interest in AFM viscosity measurements of liquids is in measuring the viscosity of liquid boundary layers at solids. The question that we are faced with is whether the AFM is

sensitive enough to detect forces at the tip. Previously, we showed that for liquid confinements of a polymer brush system, the force modulated force displacement measurements are sensitive to the very end of the cantilever tip [4]. Hence, the AFM is a useful tool to measure the rheological properties of simple or complex liquids with a resolution in three-dimensions on the nanometer scale. For AFM measurements in liquids, only the drag forces acting at the very end of the tip are of interest. All other drag forces acting on the bulk cantilever are providing a “background signal” which serves for calibration purposes. The “background signal” (in our case the phase shift between the input sinusoidal modulation and the output response) is related in Fig. 3 to the kinematic viscosity.

Squalane, a branched alkane, was chosen for our calibration curve because of its strong viscosity dependence on temperature and its chemical neutral behavior with the silicon surface. A first AFM calibration curve was established from standard calibration oils (measured in bulk) of different viscosities and tested with bulk squalane to determine the reliability of the squalane measurements [9]. It is important to note that this “blind” calibration method demands that subsequent measurements be conducted at the same frequency and cantilever-laser position as used during the calibration. The calibration is always established in the bulk liquid, i.e., far away from any interfaces. Our calibration curve is established from a set of bulk liquids. Water and ethanol have been chosen as simple liquids along with squalane. The calibration curve established, Fig. 3, shows a somewhat parabolic dependence of the phase shift with viscosity and is used as a “master curve” within the restrictions mentioned above for determining the bulk viscosity of any liquid, and variations in viscosity as a function of the distances to interfaces.

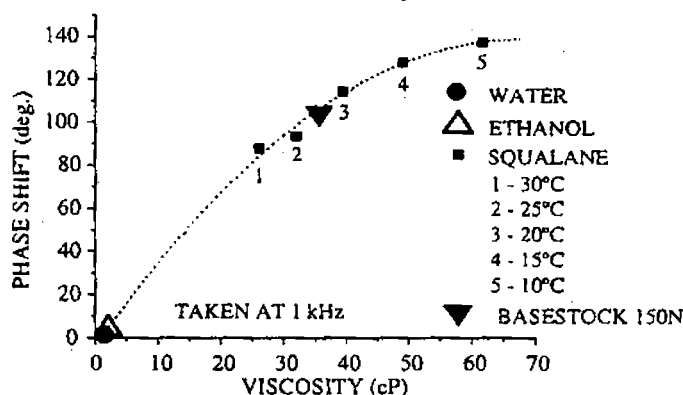


Figure 3. Liquid viscosity calibration curve based on squalane.

The target of this viscosity study is the basestock 150N, a complex mixture used as a solvent for various additives to form engine oils. The viscosity of the basestock was determined to be ~36 cP with the calibration curve of Fig 3.

In order to measure changes in viscosity in the vicinity of the solid silicon surface the cantilever is moved with a steady velocity of 20nm/s towards the surface. The steady approach is superimposed by a sinusoidal modulation of 5 nm (rms amplitude) at 1 kHz – modulated approach curve. The phase shift is recorded as a function of the cantilever displacement, Fig. 4. Modulated approach curves in the basestock and squalane at 20°C show for basestock 150N a significantly extended transition region between the bulk liquid and the solid silicon interface. It is to note that at 20°C, squalane and basestock 150N have similar kinematic viscosities (around 35-40 cP). Hence, the width of the transition region is not the result of bulk viscosity differences. We can conclude that the transition region of basestock 150N versus squalane is a measure of the molecular liquid complexity, which is responsible for the gradual change of viscosity in the vicinity of the solid interface.

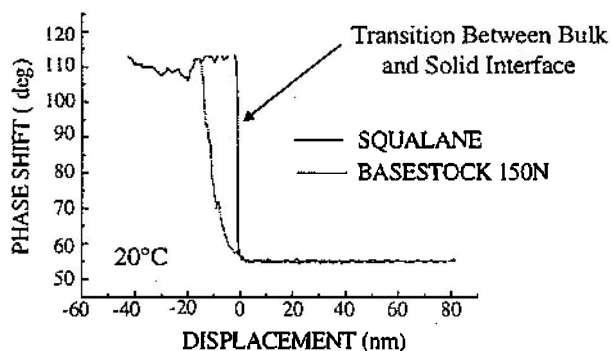


Figure 4. Modulated approached curves in liquid. Due to the molecular liquid complexity, the transition region between the bulk liquid and solid surface shows a gradual change for the basestock in comparison to the squalane.

CONCLUSIONS

We have described three simple calibration methods for lateral force, elasticity, and kinematic viscosity. A “blind” method has been introduced for friction, which reduces the calibration to a single geometry factor. The goal of this study was to provide a friction calibration method, which can easily be applied in other laboratories. In force modulation measurement, we discussed the effect of resonances on the interpretation and quantification of mechanical property results. We found it necessary to avoid AFM system resonances for a quantitative but also qualitative analyses. Finally, the AFM has been introduced as a three-dimensional rheometer. With a calibration procedure, it has been shown for modulated approach curves on liquids, with different molecular complexity but the same viscosity, that the liquid mobility at the solid interface is decreased for higher molecular complexity.

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REFERENCES

1. G. Binnig, C.F. Quate, Ch. Gerber, *Phys. Rev Lett.* **56**, 930-933 (1986).
2. C.K. Buenviaje, S. Ge, M.H. Rafailovich, J. Sokolov, J.M. Drake, C.F. Pictroski, R.M. Overney, *Langmuir*, submitted (1998).
3. R.M. Overney, E. Meyer, J. Frommer, H.-J. Guentherodt, M. Fujihira, H. Takano, Y. Gotoh, *Langmuir* **10**, 1281-1286 (1994).
4. R.M. Overney, D.P. Leta, C.F. Pictroski, M.H. Rafailovich, Y. Liu, J. Quinn, J. Sokolov, A Eisenberg, G. Overney, *Phys. Rev Lett.* **76**, 1272-1275 (1996).
5. R.M. Overney, L. Guo, H. Totsuka, M. Rafailovich, J. Sokolov, S.A. Schwarz, *Mat. Res. Soc. Symp. Proc.* **464**, 133-144 (1997).
6. J.L. Hutter, J. Bechhoefer, *Rev. Sci. Instrum.* **64**, 1868-1873 (1993).
7. J. Cleveland, S. Manne, D. Bocek, P.K. Hansma, *Rev. Sci. Instrum.* **64**, 403-405 (1993).
8. W. Kiridena, V. Jain, P.K. Kuo, G. Liu, *SIA* (in press).
9. R.M. Overney and J.M. Drake, (work in progress).