

Quantitative force measurements in liquid using frequency modulation atomic force microscopy

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The measurement of short-range forces with the atomic force microscope (AFM) typically requires implementation of dynamic techniques to maintain sensitivity and stability. While frequency modulation atomic force microscopy (FM-AFM) is used widely for high-resolution imaging and quantitative force measurements in vacuum, quantitative force measurements using FM-AFM in liquids have proven elusive. Here we demonstrate that the formalism derived for operation in vacuum can also be used in liquids, provided certain modifications are implemented. To facilitate comparison with previous measurements taken using surface forces apparatus, we choose a model system (octamethylcyclotetrasiloxane) that is known to exhibit short-ranged structural ordering when confined between two surfaces. Force measurements obtained are found to be in excellent agreement with previously reported results. This study therefore establishes FM-AFM as a powerful tool for the quantitative measurement of forces in liquid. © 2004 American Institute of Physics. [DOI: 10.1063/1.1803932]

The versatility of the atomic force microscope (AFM) has led to its widespread application in molecular and atomic scale imaging¹ and sensitive force measurements.² The simplest and most common technique used for quantitative force measurements involves directly monitoring the static deflection of the cantilever, from which the force is determined using Hooke's law. However, this static technique can suffer from a "jump-into-contact" instability when compliant cantilevers are subject to short-range attractive forces, thus restricting its use. Importantly, this limitation can be overcome using dynamic measurement techniques (i.e., oscillating the cantilever) that employ stiff cantilevers and allow for equal, if not greater, measurement sensitivity in comparison to static techniques.³ For these dynamic techniques to be useful, however, it is essential that the resulting force measurements be fully quantitative. This is particularly challenging given that the measurement parameters in dynamic modes of operation, such as the change in oscillation amplitude or resonant frequency, do not correspond in a straightforward way to the interaction force, as is the case in static mode.

The most widespread dynamic method used for sensitive force measurements in liquid monitors the change in oscillation amplitude when the cantilever is driven at a frequency well below the fundamental resonance.⁴⁻⁶ To obtain quantifiable force measurements using this technique, the oscillation amplitude must be significantly smaller than all characteristic length scales of the interaction. Importantly, the change in the oscillation amplitude can be directly linked to the interaction force gradient in the limit when the oscillation amplitude approaches zero. However, this limit of infinitesi-

mal oscillation amplitude (i.e., where the oscillation amplitude is more than an order of magnitude smaller than the interaction length scale) can be difficult to achieve. Consequently, finite amplitude effects can introduce significant errors in practice.⁷

Frequency modulation atomic force microscopy (FM-AFM) is an alternative dynamic technique that employs a feedback circuit to self-excite the cantilever at its resonant frequency. The presence of an interaction force between tip and sample is then detected as a change in resonant frequency, while the presence of dissipative forces can also be detected by monitoring the change in excitation required to keep the tip amplitude constant during the interaction. While this technique has been used successfully in vacuum to conduct quantitative force measurements,⁸ such quantitative studies in liquid have proven elusive.

Recently, FM-AFM was extended and demonstrated to be a powerful technique for conducting simultaneous imaging and "qualitative" measurements of short-range forces in liquid environments.^{9,10} However, applicability of FM-AFM to quantitative force measurements in liquid and a protocol for its implementation is yet to be established and validated. In this study, we show that the methodology used for quantitative force measurements in vacuum^{8,11} is also applicable to liquid systems, provided certain modifications are introduced. To facilitate comparison to force measurements using other techniques, we choose a model system, octamethylcyclotetrasiloxane (OMCTS), exhibiting short-range oscillatory forces in liquid. This liquid has proved to be one of the easiest in which to observe ordering of liquid molecules using both AFM⁴ and surface forces apparatus (SFA).¹² Importantly, the short-range nature of its layered behavior upon confinement limits the applicability of static techniques, which invariably suffer from stability issues. This problem

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underlies the limitation of previous SFA measurements, which are incapable of measuring the attractive branch of the interaction due to the loss of stability.¹² Dynamic AFM techniques can overcome this restriction and enable the complete force profile to be probed.

We now detail means for implementing FM-AFM in the quantitative measurement of forces in liquid. In FM-AFM, the change in resonant frequency and excitation amplitude, at constant tip amplitude, is monitored. In contrast to operation in vacuum, excitation of the cantilever in liquid by vibrating its base (e.g., piezo activation) is problematic, since it introduces unwanted resonance peaks that are not related to the true dynamics of the cantilever. To overcome this problem, the cantilever is excited directly by attaching a small magnetic particle to its end, and driving with a solenoid positioned under the sample. This enables the unequivocal determination of the resonant frequency by removing unwanted resonance peaks that occur when the tip is oscillated using piezo activation. To convert the observed frequency shift into an interaction force $F(z)$, the formulation recently proposed by Sader and Jarvis¹¹ is used

$$F(z) = 2k \int_z^\infty \left(1 + \frac{A^{1/2}}{8\sqrt{\pi(t-z)}} \right) \Omega(t) - \frac{A^{3/2}}{\sqrt{2(t-z)}} \frac{d\Omega(t)}{dt} dt, \quad (1)$$

where k is the spring constant, A is the oscillation amplitude of the tip, $\Omega(z) = \Delta\omega(z)/\omega_{\text{res}}$, ω_{res} the natural resonant frequency of the cantilever in the absence of an interaction force, and z is the distance of closest approach between the tip and the surface. Equation (1) is chosen since it is valid irrespective of the oscillation amplitude A and the nature of the force.

It is well known that the resonant frequency of the cantilever in liquid can differ significantly from its value in vacuum. For the above formulation to be valid, the specified resonant frequency ω_{res} in Eq. (1) is the value when there is no interaction force $F(z)$ between tip and sample, and the cantilever is in close proximity to the surface, i.e., when the tip-sample separation is much smaller than tip height. In this case, the inertial hydrodynamic loading of the cantilever, and hence ω_{res} is not modified as the cantilever tip approaches the surface, since only the squeeze film damping between the tip and sample is significantly affected.

Freshly cleaved highly oriented pyrolytic graphite was chosen for the sample substrate and imaged using constant excitation^{9,10} prior to performing frequency shift versus tip-sample separation measurements in order to select a suitably flat region. To minimize hydrodynamic effects of the bulk standard AFM tip, we used a multi-walled carbon nanotube as the probing tip. The carbon nanotube was attached to the tip of a standard AFM cantilever (Nanosensor EFM Cantilever), with spring constant 3 N/m, using a manipulator positioned inside a scanning electron microscope.¹⁵ A magnetic particle was glued onto the backside of the cantilever to enable magnetic activation.⁹ The resonant frequency of the cantilever (with magnetic particle attached) was found to be 28.19 kHz in air. When immersed in OMCTS and in close proximity to the surface (50 nm tip-sample separation), a resonant frequency of 19.54 kHz was measured, i.e., $\omega_{\text{res}} = 2\pi 19.54 \times 10^3$ rad/s, and used in Eq. (1). Au measurements were made on a modified Asylum Research MFP-3D SA AFM.

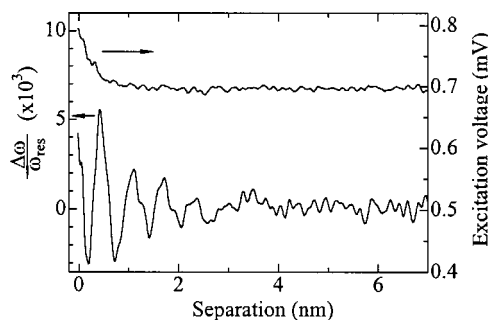


FIG. 1. Typical frequency shift (left axis) and excitation amplitude (right axis) curves during tip-sample approach. Oscillation amplitude of cantilever is 2.0 nm. Period of the oscillatory force is 0.73 nm. The maximum number of layers observed is four.

Figure 1 shows a typical frequency shift and excitation signal (voltage applied to the coil driver in order to keep the oscillation amplitude of the cantilever constant at $A = 2.0$ nm) as a function of separation. Oscillations observed in the frequency shift indicate the ordering of OMCTS molecules at the interface; in this case, four molecular layers were detected. Analysis of 132 measurements showing oscillations revealed a mean spacing of 0.73 ± 0.08 nm between two oscillation peaks. This value is in good agreement with previous SFA experiments that measured a spacing of 0.82 ± 0.02 nm¹⁴ and with theoretical values predicted by a hard sphere model.¹⁴ In contrast to the frequency shift curves, the excitation signal increases monotonically as the tip approaches the surface and appears to be insensitive to layering in the OMCTS.

To validate the FM-AFM technique in liquid, it is essential to demonstrate that identical interaction force laws are recovered irrespective of the magnitude of oscillation amplitude. To test this requirement, we measured frequency shift versus separation curves using a range of oscillation amplitudes, $A = 2.0, 3.9, 7.2$ nm as shown in Fig. 2.¹⁵ These frequency shift curves correspond to cases where the oscillation amplitude was comparable to or significantly greater than the characteristic length scale of the interaction (i.e., the diameter of an OMCTS molecule). From Fig. 2, it is clear that the change in resonant frequency decreases as the oscillation amplitude A is increased. This behavior is expected, since a shorter proportion of the oscillation cycle experiences an interaction force, as the oscillation amplitude increases. This finding also agrees with observations taken on different systems in vacuum.³ From Fig. 2, it is also noted that the noise level in the frequency shift is reached for separations greater than ~ 3 nm. Given that an increase in oscillation amplitude

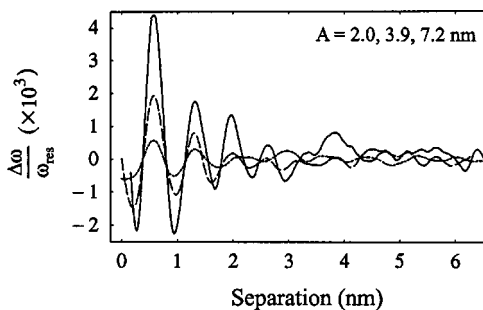


FIG. 2. Frequency shift vs separation curves obtained using a range of oscillation amplitudes, $A = 2.0$ nm (solid), $A = 3.9$ nm (dashed), $A = 7.2$ nm (dotted).

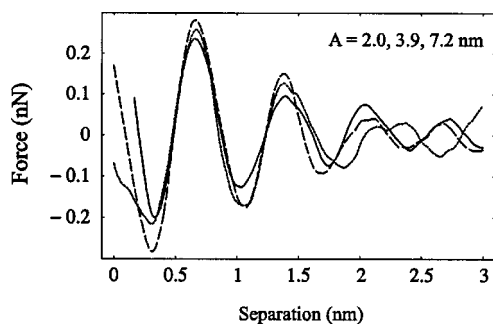


FIG. 3. Force vs separation results obtained from data in Fig. 2 using Eq. (1). Results given for all three oscillation amplitudes, $A=2.0$ nm (solid), $A=3.9$ nm (dashed), $A=7.2$ nm (dotted).

decreases the frequency shift, the frequency noise floor is reached at smaller separations for greater oscillation amplitudes.

Next we use Eq. (1) to convert these frequency shift curves into an interaction force for separations less than 3 nm, the results of which are given in Fig. 3. It is strikingly evident that the same force law is recovered irrespective of the oscillation amplitude used. We note that some adjustment of the absolute separation was made to compensate for the fact that zero separation is not accurately defined or measured in the AFM. Nonetheless, it is clear that while the frequency shift shows dramatic changes as a function of oscillation amplitude, the recovered force law is insensitive to the oscillation amplitude chosen, cf. Figs. 2 and 3. Specifically, we note that the first two peaks in the interaction force superimpose well at all oscillation amplitudes, while some discrepancy exists for the third and fourth peaks between measurements for oscillation amplitude 7.9 nm and those of the lower two oscillation amplitudes. This finding is commensurate with a loss in sensitivity of the highest oscillation amplitude measurement at separations lower than 3 nm.

To complete our validation of the FM-AFM technique in liquid, it is necessary to compare these force results to previously obtained independent measurements. Here, we compare our measurements to those obtained previously with SFA^{12,14} which utilizes interaction areas many orders of magnitude greater than the one used here (i.e., number of interacting molecules in the SFA is typically a factor of 10^{12} greater than in this FM-AFM measurement). Specifically, the radius of curvature of the mica sheets used in SFA is ~ 1 cm, whereas the radius of our carbon nanotube tips, measured in an SEM, is 15 ± 5 nm. Nonetheless, if the force is normalized by the corresponding radius, similar results are obtained using both SFA and FM-AFM, with typical peak normalized forces ~ 10 mN/m being observed. A normalized force curve obtained using an oscillation amplitude of 2.0 nm is shown in Fig. 4. It is also interesting to compare the decay length of the oscillatory forces over each period. The force value measured at the peak of each layer was found to decrease exponentially with separation, with a decay length of 1.1 nm, see inset of Fig. 4. This is similar to the decay length measured by SFA, which was found to be 1.2–1.7 molecular diameters.¹² These findings are particularly significant, since they demonstrate that measurements over macroscopic and nanometer scale interaction areas coincide well for this system. We therefore deduce that there is no significant lateral

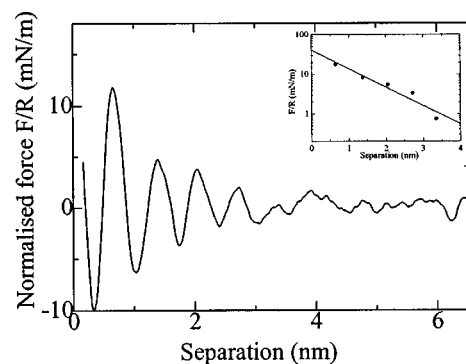


FIG. 4. Normalized force (force F /tip radius R) using carbon nanotube (radius = 15 nm) and cantilever oscillation amplitude $A=2.0$ nm. Results enable comparison with existing SFA data. The inset shows the peak forces of the oscillation as a function of tip-sample separation. The exponential decay length is 1.1 nm.

variation in OMCTS liquid layering on the nanoscale for these surfaces, nor is the layering significantly modified by the difference in surface chemistry from mica (in the case of SFA) to carbon (in the case of our measurements). In other words, the ordering of OMCTS molecules is predominantly the result of confinement due to geometry rather than a localized bonding effect due to chemistry.

In summary, we have established that FM-AFM can be used to conduct quantitative force measurements in liquid. This was achieved by presenting a rigorous formalism for its implementation that was subsequently validated by examining a model liquid system (octamethylcyclotetrasiloxane) exhibiting short-range interactions under confinement. Excellent agreement with independent measurements made using SFA was found.

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¹F. J. Giessibl, *Science* **267**, 68 (1995).

²D. Fotiadis, S. Scheuring, S. A. Müller, A. Engel, and D. J. Müller, *Micron* **33**, 385 (2002).

³R. Garcia and R. Perez, *Surf. Sci. Rep.* **47**, 197 (2002).

⁴S. J. O'Shea, M. E. Welland, and J. B. Pethica, *Chem. Phys. Lett.* **223**, 336 (1994).

⁵W. Han and S. M. Lindsay, *Appl. Phys. Lett.* **72**, 1656 (1998).

⁶M. Antognozzi, A. D. Humphris, and M. J. Miles, *Appl. Phys. Lett.* **78**, 300 (2001).

⁷P. M. Hoffmann, *Appl. Surf. Sci.* **210**, 140 (2003).

⁸M. A. Lantz, H. J. Hug, R. Hoffmann, P. J. A. van Schendel, P. Kappenberger, S. Martin, A. Baratoff, and H.-J. Guntherodt, *Science* **291**, 2580 (2001).

⁹S. P. Jarvis, T. Uchihashi, T. Ishida, H. Tokumoto, and Y. Nakayama, *J. Phys. Chem. B* **104**, 6091 (2000).

¹⁰S. P. Jarvis, T. Ishida, T. Uchihashi, Y. Nakayama, and H. Tokumoto, *Appl. Phys. A: Mater. Sci. Process.* **72**, S129 (2001).

¹¹J. E. Sader and S. P. Jarvis, *Appl. Phys. Lett.* **84**, 1801 (2004).

¹²R. G. Horn and J. N. Israelachvili, *J. Chem. Phys.* **75**, 1400 (1981).

¹³H. Nishijima, S. Akita, Y. Nakayama, K. Hohmura, H. Yoshimura, and K. Takeyasu, *Appl. Phys. Lett.* **74**, 4061 (1991).

¹⁴P. Attard and J. L. Parker, *J. Phys. Chem.* **96**, 5086 (1992).

¹⁵Frequency data are smoothed to facilitate conversion using Eq. (1), since the numerical derivative must be computed in Eq. (1), cf. Figs. 1 and 2.