

Artifact-free dynamic atomic force microscopy reveals monotonic dissipation for a simple confined liquid

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We present definitive interaction measurements of a simple confined liquid (octamethylcyclotetrasiloxane) using artifact-free frequency modulation atomic force microscopy. We use existing theory to decouple the conservative and dissipative components of the interaction, for a known phase offset from resonance (90° phase shift), that has been deliberately introduced into the experiment. Further we show the qualitative influence on the conservative and dissipative components of the interaction of a phase error deliberately introduced into the measurement, highlighting that artifacts, such as oscillatory dissipation, can be readily observed when the phase error is not compensated for in the force analysis. © 2008 American Institute of Physics.

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The confinement of a liquid between two approaching bodies has received considerable attention in order to understand processes concerning tribology,¹ geoscience,² catalysis, and biological function.^{3,4} When a liquid is confined between two surfaces, the liquid molecules at the nanometer scale behave differently to those in the bulk liquid, ordering into discrete layers called solvation shells due to the presence of an interaction with the solid surfaces.⁵ The resulting solvation force has been measured extensively using the surface force apparatus^{6,7} (SFA) and the atomic force microscope^{8,9} (AFM) and shows an oscillatory profile as a function of the separation between the two surfaces. With both measurement systems, dynamic measurements have been possible, allowing dissipative components of the interaction to be measured in the near surface region. However, in the case of dissipation the results have been far less consistent than for the readily observed oscillatory conservative force profile.

A recent letter on the confinement of a simple liquid using tapping mode AFM, showed clear oscillations in the measured dissipation and effective viscosity as a function of tip-sample separation.¹⁰ The authors stated that the high sensitivity of the measurements were able to reveal oscillations in the measured dissipation, differing from earlier observations where the dissipation has been reported to increase monotonically with decreasing tip-sample separation.¹¹ A comment later published in response to the data presented in the letter, suggested that from a theoretical perspective, if the measurements were not made at the true resonance frequency (i.e., with a phase error), this could introduce artifacts in the dissipation measurements due to the coupling of the conservative and dissipative interactions away from resonance.¹² This has also been clearly highlighted in a theoretical article that introduces a mathematical decoupling when the phase error is known.¹³

Here we present definitive measurements investigating whether an experimental error in the phase does indeed introduce qualitative artifacts in the measured data, due to the coupling of the conservative and dissipative components of the interaction. We have chosen to study the confinement of

octamethylcyclotetrasiloxane (OMCTS) between the AFM tip and the solid surface, as this is a model system that has been investigated extensively.^{5,7,8} We have used frequency modulation AFM (FM-AFM) as this does not suffer from the bistability inherent with the amplitude modulation technique. Magnetic activation dynamic (MAD) mode¹⁴ was also used in order to eliminate unwanted resonance peaks and phase shifts, which are characteristic of alternative activation methods. The resonant frequency of the cantilever has been experimentally determined with a high precision, such that phase error can be accurately controlled.

The FM-AFM measurements on the confinement of OMCTS (Sigma) between an AFM tip and a freshly cleaved highly oriented pyrolytic graphite surface (NT-MDT) were performed using a modified SA MFP-3D™ AFM (Asylum Research, Santa Barbara, CA) for MAD mode. PPP-FM cantilevers (Nanosensors, Switzerland), with a typical spring constant of 2.0 N/m were used. To implement MAD mode, a magnetic particle was attached to the back of the cantilever with the aid of a light microscope and a micromanipulator. A thermal noise spectrum of the cantilever in liquid at a 100 nm tip-sample separation was taken and fit to the response of a damped harmonic oscillator¹⁵ in order to determine the true resonant frequency (ω_{res}) of the cantilever (90° phase shift). The experimentally determined resonant frequency of the cantilever-magnet assembly in liquid was 20 251 Hz, with a Q factor of 2.8. The experimental precision in determining the resonant frequency was 0.5%. Knowledge of the resonant frequency at a specific tip-sample separation ensures that if any significant changes in the resonant frequency occur, they can be detected accurately and accounted for in the analysis of the data. An additional thermal noise spectrum was taken at the end of the experiment and the fit to this spectrum showed no significant change in the resonant frequency. The experimental uncertainty in the absolute phase value was $\pm 2^\circ$. This uncertainty is due to the speed with which the thermal noise data has to be collected in close proximity to the surface so that thermal drift does not cause the tip to actually make contact with the surface during data collection.

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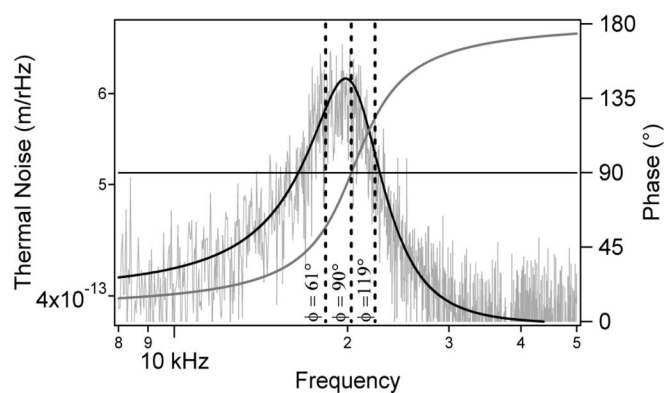


FIG. 1. The thermal noise spectrum of the AFM cantilever taken at a 100 nm tip-sample separation in liquid with the corresponding fit (black line) to the response of a damped harmonic oscillator and the corresponding theoretical phase shift (gray line). The vertical lines depict the three phase shifts used in the measurements.

For FM detection a Nanosurf PLL controller/detector (Nanosurf, Switzerland) was used to keep the cantilever oscillating at constant amplitude ($A=2.55$ nm) and at the experimentally determined resonant frequency. The changes in the resonant frequency and the excitation amplitude, at constant cantilever amplitude, were monitored to measure the frequency shift and dissipation caused by the tip-sample interaction. The phase, ϕ , was artificially offset from the true resonance by $\pm 29^\circ$ in order to investigate the effect of phase error on the coupling of the conservative and dissipative interactions. Figure 1 indicates where the three phases lie on the thermal noise spectrum of the cantilever. The raw data presented in this study are representative curves from reproducible approach and retract data, while the converted force data is based on the average of ten reproducible approach curves as the retract data show the same trends.

The frequency shift data for the three measured phase offsets show clear oscillations, due to the molecular ordering of the OMCTS molecules at the liquid-solid interface (Fig. 2). The average periodicity is 8.3 Å for measurements made on resonance and is in close agreement with previously reported values for the confinement of OMCTS between two approaching surfaces.^{5,7,8} The periodicity of the oscillation was not affected by phase error as the average periodicity was found to be similar for the three phase values. The oscillations in the frequency shift data appear to be superimposed on an attractive background, which is attributed to surface chemistry⁷ and tip geometry⁵ effects. In the case where $\phi=119^\circ$, the measured frequency shifts show oscillations that are smaller in magnitude compared to those for $\phi=90^\circ$, while they are larger in magnitude for the $\phi=61^\circ$ case. The dissipation data presented in Fig. 2 show a steep monotonic increase for the $\phi=90^\circ$ and $\phi=119^\circ$ cases, with no oscillations clearly distinguishable above the noise level. For the case where $\phi=61^\circ$, the dissipation data show distinct oscillations that are in phase with the corresponding frequency shift curve [Fig. 2(c)]. These oscillatory variations in the dissipation have been reported elsewhere,^{10,16} but based on our measurements these oscillations are considered to be artifacts of an experimental error in the phase. We have also calculated an effective viscosity¹⁰ from the damping data which show distinct oscillations in only the $\phi=61^\circ$ case. The minimum detectable effective viscosity oscillation was a

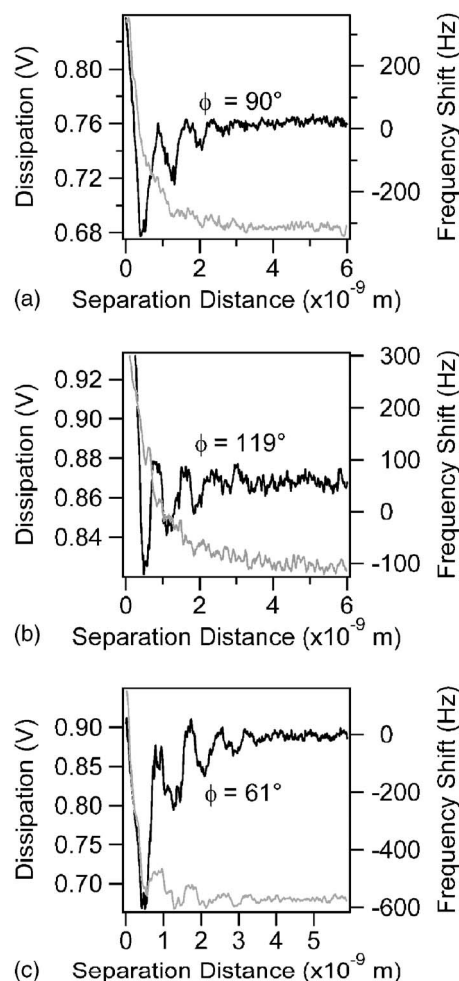


FIG. 2. Raw dissipation (gray line) and frequency shift (black line) data for $\phi =$ (a) 90° , (b) 119° , and (c) 61° .

change of 0.3 poise. The uncertainty in the measurements is of the order of 0.1 poise, which is sufficient to detect the presence of oscillations reported previously.¹⁰ If collective motions of the OMCTS molecules account for the increasing viscosity at tip-sample separations ≤ 1 nm, it would appear from Fig. 2(a) that this collective motion does not occur at larger distances, nor is it discretely influenced by the layering of the molecules perpendicular to the surface.

It is interesting to note that the dissipation data for $\phi = 119^\circ$ show a similar behavior as $\phi = 90^\circ$ (a purely monotonic increase), but differs greatly from $\phi = 61^\circ$ (shows distinct oscillatory behavior) even though the magnitude of phase detuning ($\Delta\phi = 29^\circ$) is the same for the two offsets. A comparison of the relative contributions of the conservative and dissipative components of the interaction force lends some insight to explain this behavior. Firstly, the asymmetric nature of the thermal noise spectrum (Fig. 1), shows that the uncompensated oscillation amplitude for $\phi = 119^\circ$ is smaller than that for $\phi = 61^\circ$. As a result, a larger driving force is required keep to the cantilever oscillating at a constant amplitude for the $\phi = 119^\circ$ case. This equates to a larger dissipative component in the coupling for $\phi = 119^\circ$ as compared to $\phi = 61^\circ$, and provides an explanation for the differences in dissipation data for the two offsets. We see oscillations in the dissipation data for $\phi = 61^\circ$, due a larger relative contribution of the conservative component in the coupling compared to $\phi = 119^\circ$.

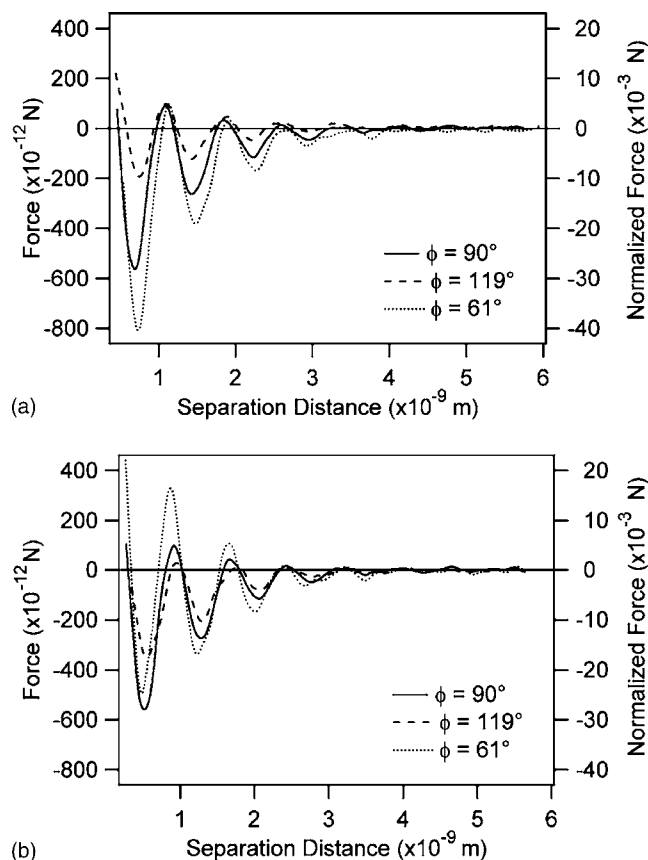


FIG. 3. The recovered force data from the frequency shift curves for three values of phase for both (a) no decoupling and (b) decoupling analysis.

The force $F(z)$ was recovered from the observed frequency shift data using the formula proposed by Sader and Jarvis,¹⁷ which is applicable to all frequency shift data, irrespective of the oscillation amplitude and the range of the interaction. In addition, we have utilized theory that has been proposed to decouple the conservative and dissipative interactions, based on relative frequency shifts and the change in the excitation amplitude (i.e., provided the phase offset is known, the conservative and dissipative interactions can be formally decoupled).¹³ The recovered force is presented for the no decoupling and decoupling cases, where no decoupling refers to the analysis of the data where the deviation from resonance ($\phi=90^\circ$) is ignored, while for the decoupling analysis, the phase error contribution has been accounted for in the analysis.

In Fig. 3(a) the recovered force using only the frequency to force conversion without any decoupling analysis, shows that the attractive background onto which the oscillations are superimposed, decreases as the phase offset extends from negative to positive. Importantly, this indicates that uncorrected phase error can also cause a qualitative change in the apparent background term, which would normally be associated with the surface chemistry and morphology. In addition, the amplitude of the oscillations is larger for $\phi=61^\circ$, followed by $\phi=90^\circ$ and lastly $\phi=119^\circ$, indicating that phase error also introduces quantitative variations in the absolute values of the force recovered. Figure 3(b) confirms that there

is no significant variation between the recovered forces for the different frequency offsets, when the decoupling method of analysis is used (we observe a slight increase in recovered force during the course of the experiment which we attribute to a slight increase in tip radius). This is particularly true for the force recovered for the first three oscillations. These experimental results verify the theory proposed by Sader and Jarvis,¹³ where the conservative and dissipative forces can be formally decoupled, provided that the phase offset is known. We note that similar measurements made with piezoactivation could not be decoupled using the proposed theory due to unpredicted phase changes resulting from the phase response of the piezoexcitation assembly.

In summary, we have presented definitive measurements of the conservative and dissipative interactions for a simple confined liquid. A typical oscillatory force profile was observed with a periodicity associated with the molecular diameter of the liquid molecules, regardless of the degree of phase offset. These oscillations were superimposed on an attractive background, the extent of which was found to be dependent on the induced phase error in the measurements. The measured dissipation showed a monotonic increase as a function of tip-sample separation for measurements made without phase error, while measurements made below resonance showed oscillations in the dissipation, which are shown to be artifacts due to the coupling of the conservative interaction with the dissipative interactions. We anticipate that the implementation of artifact free measurements will resolve apparently contradictory results in literature and provide insights into the response of simple and complex confined fluids.

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