First Ten Ångstroms

Milk as an Example of Dynamic Interfacial Tension and Dilational Stress Measurements

5 November 2003

Milk is an easy-to-obtain sample that exhibits interesting dilational stress behavior. Dilational stress parameters are obtained by periodically perturbing the surface area of a pendant drop and measuring the resultant change in interfacial tension. These parameters include interfacial elasticity and viscosity and are important in the formation and stability of foams and emulsions. In the case of milk, proteins adsorb to the surface and form a film (a “skim”) that has these properties.

2% milkfat content milk was obtained from a grocery and diluted 1000:1 with distilled water. The dilution lowered the protein concentration and made the film take longer to form, which in turn allowed us to observe it more easily.

In general, with a dilute solution, we expect the initial interfacial tension to be that of the solvent, water, and for it to gradually decrease as the film forms since, in this case, the proteins act as surfactants. We want to watch this change take place.

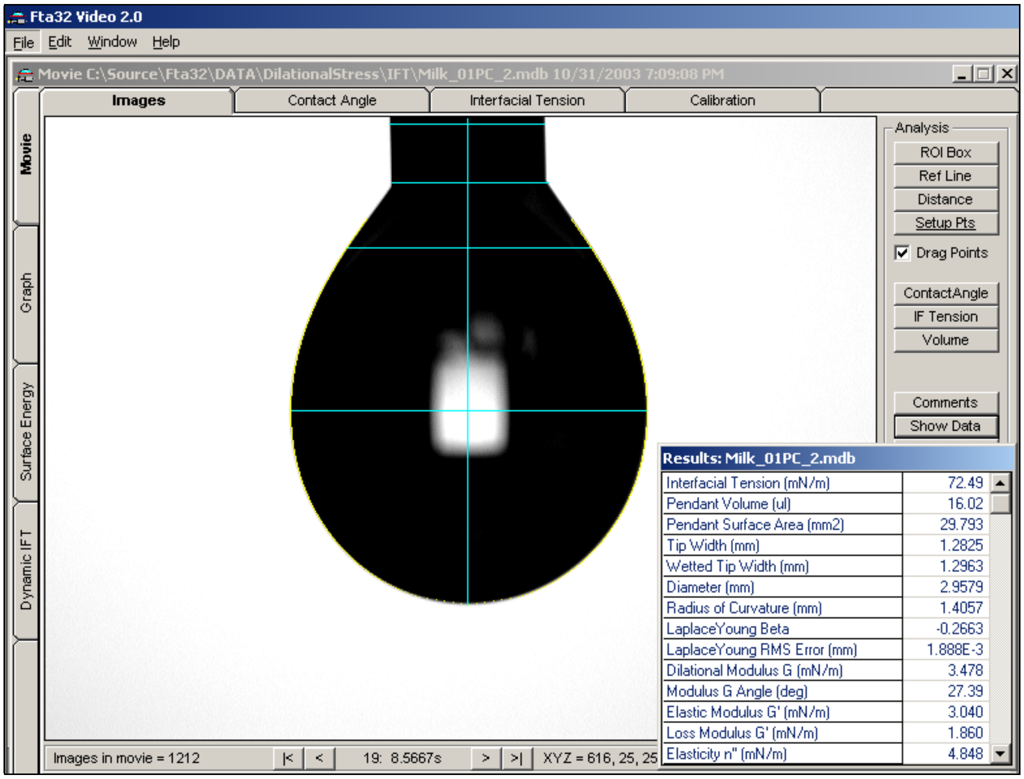
Method

The details of these measurements are discussed in the FTA paper “Dynamic Surface Tension and Dilational Stress Using the Drop Shape Method”, available at www.firsttenangstroms.com. The work reported here used a standard FTA200 instrument with a 500µl Hamilton syringe and a 18GA (1.27mm nominal outside diameter) stainless steel needle. The pendant drop was formed by starting with a just visible drop and then aggressively dispensing approximately 15µl at 5µl/s. Immediately after this the drop perturbation began and data acquisition started. The drop formation and perturbation were automatically controlled from a pump program running in the FTA software. For further details see the Checklist as the end of this paper.

The next questions are the frequency and amplitude of the perturbation. Because we wanted to compare with some previous work, we chose a 10s cycle time and a small perturbation. The dilational stress calculation uses the pendant drop surface area as an input, but we program the pump in terms of volume, so there is a bit of trial-and-error to get the desired surface area pertubation. However the calculation is not sensitive to the exact perturbation (it measures the actual perturbation and normalizes the results). The example we show ran an *amplitude* of 3.5% surface area perturbation. Terminology is important here. The calculation uses a sinusoidal fit of the measured time varying surface area and interfacial tension. The amplitude we refer to is the amplitude of this sine wave, using the definition from mathematics. But what humans "see" when they look at time plots is the peak-to-peak amplitude. Therefore we list both the (sinusoidal) amplitude, in this case 3.5%, and the peak-to-peak amplitude, in this case 2 × 3.5 = 7%. This surface area change was obtained with a change in volume of approximately 1.5µl with the 15µl drop.

The results presented here used no cuvette or chamber for the drop nor an air table for the instrument, both of which will normally lower noise levels. We will present the milk results next and then some validation runs on pure water.

Milk Results

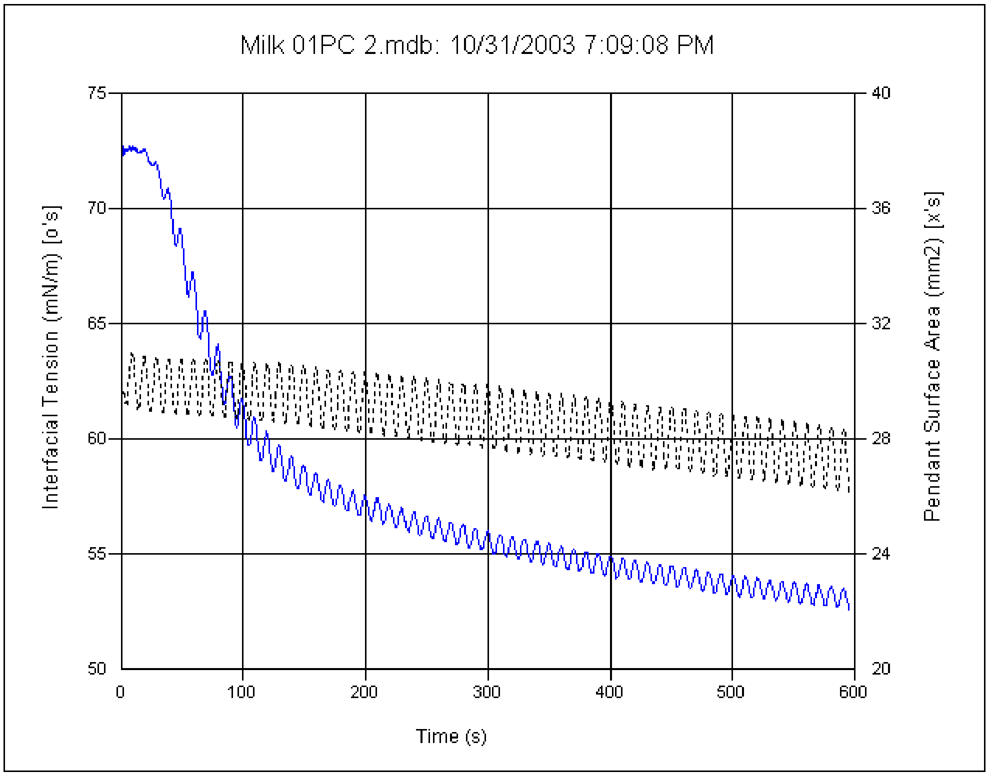


Results: Milk_01PC_2.mdb

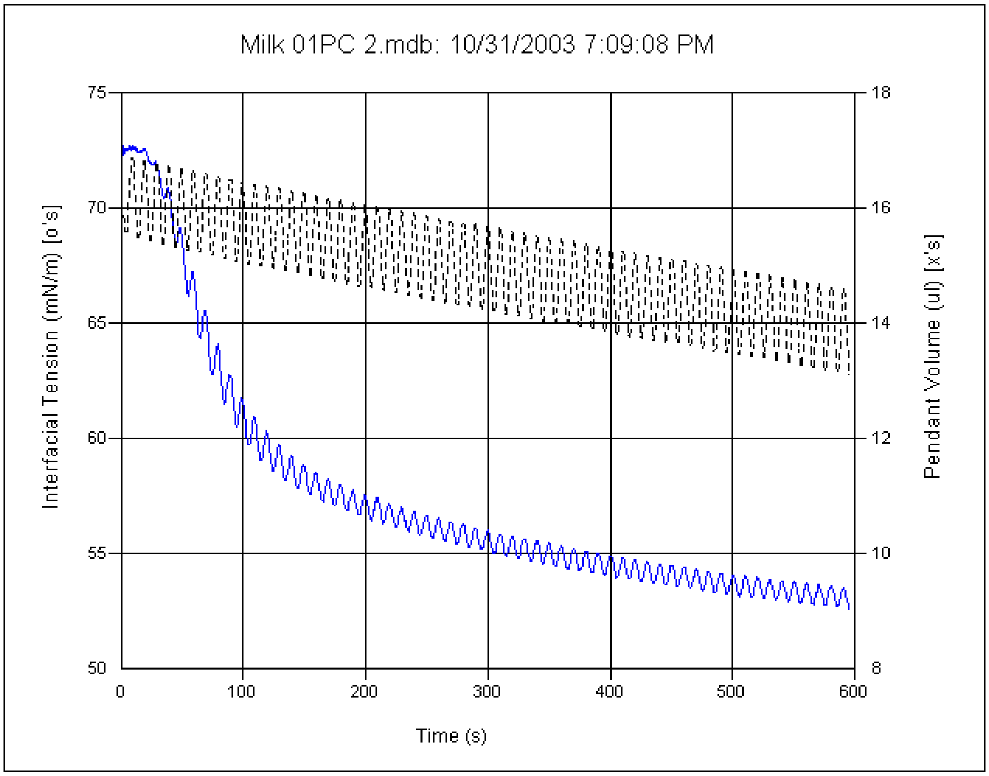
Interfacial Tension (mN/m)	72.49
Pendant Volume (ul)	16.02
Pendant Surface Area (mm2)	29.793
Tip Width (mm)	1.2825
Wetted Tip Width (mm)	1.2963
Diameter (mm)	2.9579
Radius of Curvature (mm)	1.4057
LaplaceYoung Beta	-0.2663
LaplaceYoung RMS Error (mm)	1.888E-3
Dilational Modulus G (mN/m)	3.478
Modulus G Angle (deg)	27.39
Elastic Modulus G' (mN/m)	3.040
Loss Modulus G' (mN/m)	1.860
Elasticity n" (mN/m)	4.848

Pendant drop IFT showing Laplace-Young integration and residual.

The above figure is a representative pendant drop image of the diluted milk sample. The first plot is of the interfacial tension and pendant drop surface area over the 600s duration of the run. Data point symbols were turned off in the plot to make the details of the curves visible. The surface area curve is the sinusoidal curve. Its average value has a small negative slope from evaporation. The interfacial tension curve starts near 72.5, the pure solvent value, and decreases in time to about 53mN/m. The imposed sine wave on the interfacial tension curve is the consequence of the change in surface area and is what we want to measure. A similar plot of interfacial tension and the drop volume follows. No smoothing or filtering was used on any of the data plotted. Note the graphs are autoscaled.



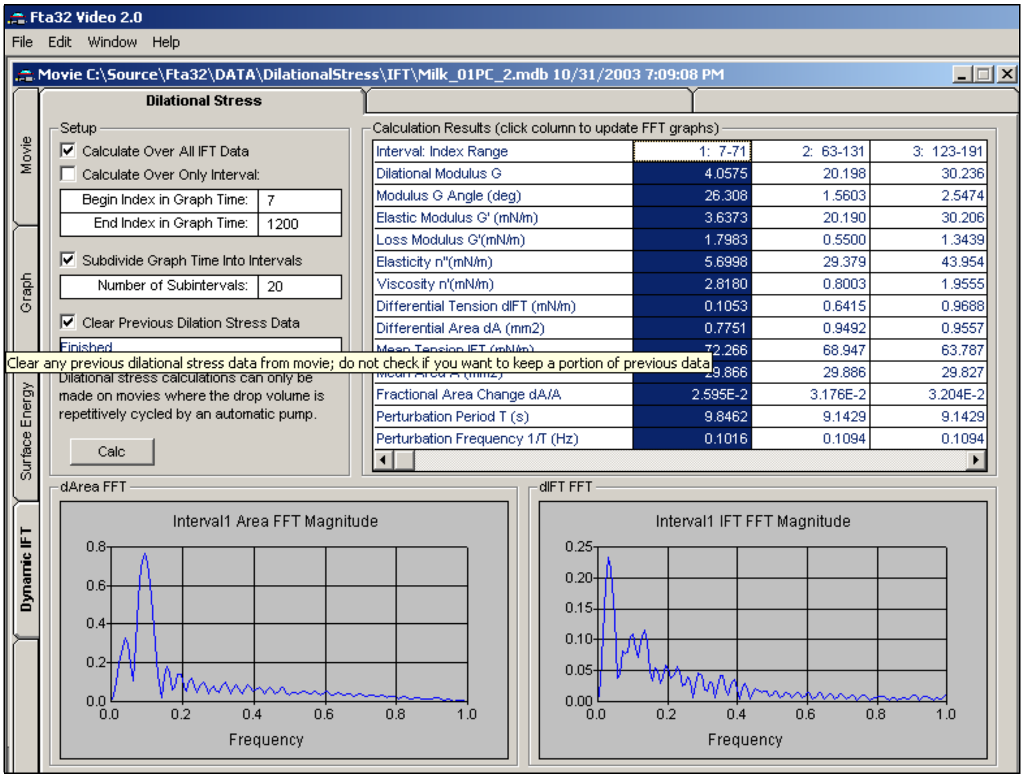
Interfacial tension and surface area.



Interfacial tension and volume.

We next show a set of screen shots from the software which will illustrate the calculation of the dilational stress parameters using fast Fourier transform (FFT) techniques. The advantage of this approach is that the transform naturally performs an optimal fit to each frequency component and we simply need to use the Fourier coefficients for the frequency component that represents the surface area perturbation. A second, technical, advantage is that the phase angle between the area and interfacial tension is easily and accurately obtained from the transforms directly because they are complex quantities and naturally have an angle. But what we plot are the magnitudes of these complex values. We chose to subdivide the overall run into 20 intervals so that we can trace the changes as the film grows. The data was sampled (an image captured and analyzed) each ½ second, so there were 20 samples in the 10s cycle. The 600s run had, therefore, about 60 perturbation cycles. This means each of the above intervals had about 3 cycles. We say "about" because the intervals are overlapped slightly to smooth the final data; this can be seen in the range for each interval listed at the top of the interval's column in the table.

We show the table and the Fourier transform plots for the area and interfacial tension functions for each selected interval. The first, 1/3, 2/3, and last intervals are shown to give a representative feel for the tabular results. The peak in the area transform is at approximately 0.1Hz, as we would expect. The algorithm finds that peak and then uses the interfacial tension value for precisely the same frequency. In this case, the interfacial tension peak value (at this frequency) is 0.105mN/m. This is the amplitude of the Fourier component (i.e., the best fit) at this frequency. This value can be seen in the IFT graph (at about 0.1Hz). Note that if we were to look at the time plot, we would "see" a sinusoid of peak-to-peak amplitude ≈0.21mN/m.



Movie C:\Source\Fta32\DATA\DilationalStress\IFT\Milk_01PC_2.mdb 10/31/2003 7:09:08 PM

Setup

☑ Calculate Over All IFT Data

☐ Calculate Over Only Interval:

Begin Index in Graph Time:	7
End Index in Graph Time:	1200

☑ Subdivide Graph Time Into Intervals

Number of Subintervals:	20

☑ Clear Previous Dilation Stress Data

Finished

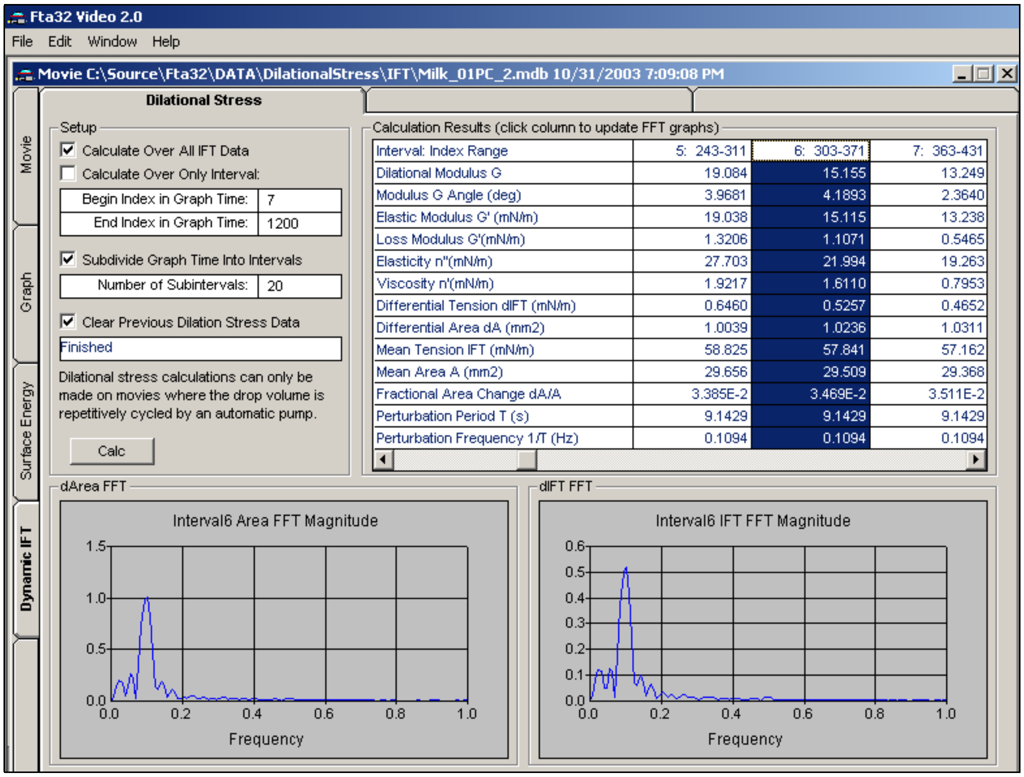
Clear any previous dilational stress data from movie; do not check if you want to keep a portion of previous data

Dilational stress calculations can only be made on movies where the drop volume is repetitively cycled by an automatic pump.

Calculation Results (click column to update FFT graphs)

Interval: Index Range	1: 7-71	2: 63-131	3: 123-191
Dilational Modulus G	4.0575	20.198	30.236
Modulus G Angle (deg)	26.308	1.5603	2.5474
Elastic Modulus G' (mN/m)	3.6373	20.190	30.206
Loss Modulus G'(mN/m)	1.7983	0.5500	1.3439
Elasticity n"(mN/m)	5.6998	29.379	43.954
Viscosity n'(mN/m)	2.8180	0.8003	1.9555
Differential Tension dIFT (mN/m)	0.1053	0.6415	0.9688
Differential Area dA (mm2)	0.7751	0.9492	0.9557
Mean Tension IFT (mN/m)	72.266	68.947	63.787
Mean Area A (mm2)	29.866	29.886	29.827
Fractional Area Change dA/A	2.595E-2	3.176E-2	3.204E-2
Perturbation Period T (s)	9.8462	9.1429	9.1429
Perturbation Frequency 1/T (Hz)	0.1016	0.1094	0.1094

First interval; modulus G = 4.06mN/m, a relatively low number.



Movie C:\Source\Fta32\DATA\DilationalStress\IFT\Milk_01PC_2.mdb 10/31/2003 7:09:08 PM

Setup

☑ Calculate Over All IFT Data

☐ Calculate Over Only Interval:

Begin Index in Graph Time: 7

End Index in Graph Time: 1200

☑ Subdivide Graph Time Into Intervals

Number of Subintervals: 20

☑ Clear Previous Dilation Stress Data

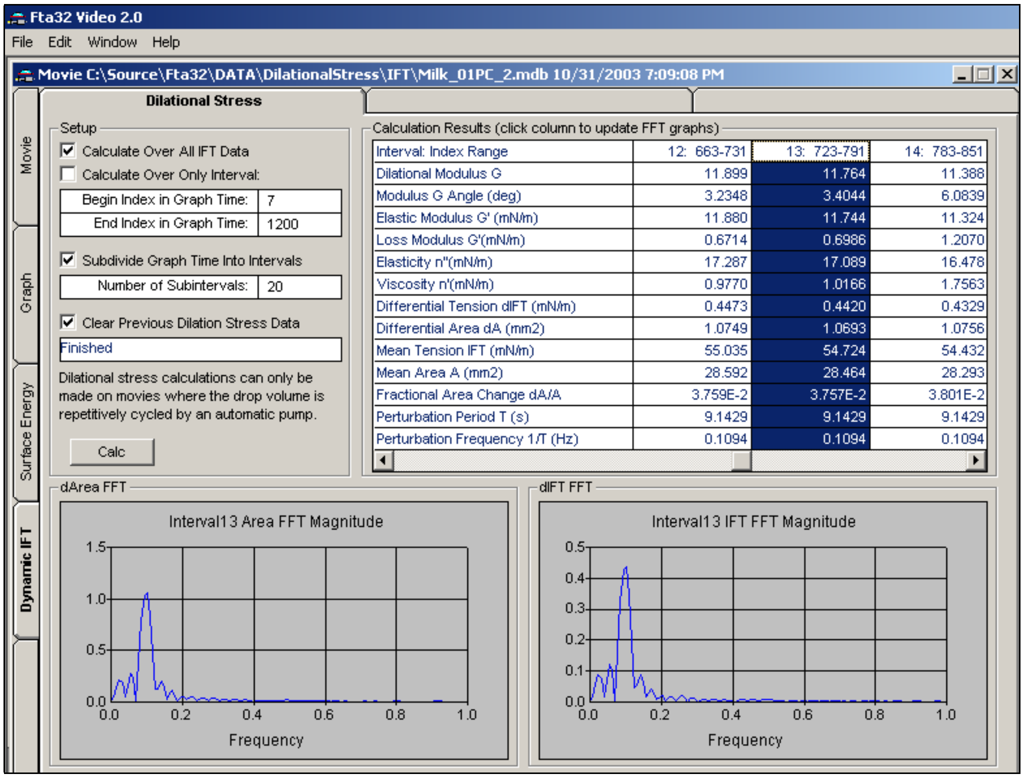
Finished

Dilational stress calculations can only be made on movies where the drop volume is repetitively cycled by an automatic pump.

Calculation Results (click column to update FFT graphs)

Interval: Index Range	5: 243-311	6: 303-371	7: 363-431
Dilational Modulus G	19.084	15.155	13.249
Modulus G Angle (deg)	3.9681	4.1893	2.3640
Elastic Modulus G' (mN/m)	19.038	15.115	13.238
Loss Modulus G'(mN/m)	1.3206	1.1071	0.5465
Elasticity n"(mN/m)	27.703	21.994	19.263
Viscosity n'(mN/m)	1.9217	1.6110	0.7953
Differential Tension dIFT (mN/m)	0.6460	0.5257	0.4652
Differential Area dA (mm2)	1.0039	1.0236	1.0311
Mean Tension IFT (mN/m)	58.825	57.841	57.162
Mean Area A (mm2)	29.656	29.509	29.368
Fractional Area Change dA/A	3.385E-2	3.469E-2	3.511E-2
Perturbation Period T (s)	9.1429	9.1429	9.1429
Perturbation Frequency 1/T (Hz)	0.1094	0.1094	0.1094

Sixth interval; interfacial tension peak has grown in magnitude.



Movie C:\Source\Fta32\DATA\DilationalStress\IFT\Milk_01PC_2.mdb 10/31/2003 7:09:08 PM

Setup

☑ Calculate Over All IFT Data

☐ Calculate Over Only Interval:

Begin Index in Graph Time: 7

End Index in Graph Time: 1200

☑ Subdivide Graph Time Into Intervals

Number of Subintervals: 20

☑ Clear Previous Dilation Stress Data

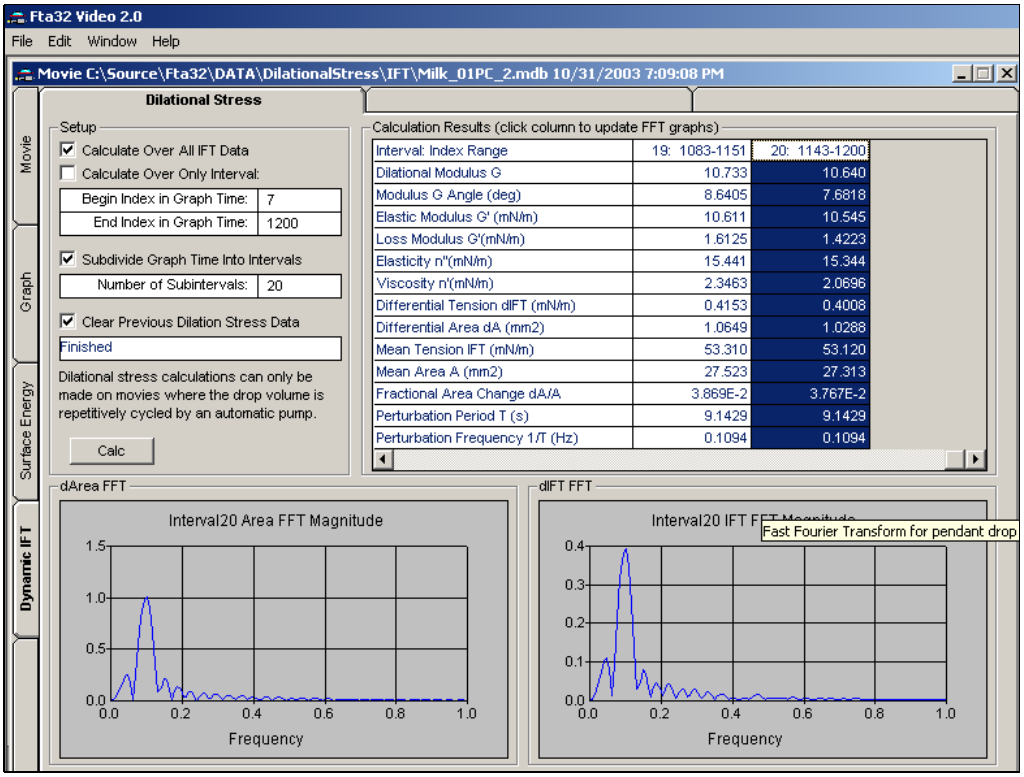
Finished

Dilational stress calculations can only be made on movies where the drop volume is repetitively cycled by an automatic pump.

Calculation Results (click column to update FFT graphs)

Interval: Index Range	12: 663-731	13: 723-791	14: 783-851
Dilational Modulus G	11.899	11.764	11.388
Modulus G Angle (deg)	3.2348	3.4044	6.0839
Elastic Modulus G' (mN/m)	11.880	11.744	11.324
Loss Modulus G'(mN/m)	0.6714	0.6986	1.2070
Elasticity n"(mN/m)	17.287	17.089	16.478
Viscosity n'(mN/m)	0.9770	1.0166	1.7563
Differential Tension dIFT (mN/m)	0.4473	0.4420	0.4329
Differential Area dA (mm2)	1.0749	1.0693	1.0756
Mean Tension IFT (mN/m)	55.035	54.724	54.432
Mean Area A (mm2)	28.592	28.464	28.293
Fractional Area Change dA/A	3.759E-2	3.757E-2	3.801E-2
Perturbation Period T (s)	9.1429	9.1429	9.1429
Perturbation Frequency 1/T (Hz)	0.1094	0.1094	0.1094

Thirteenth interval; interfacial tension peak is not quite as tall.



Setup

☑ Calculate Over All IFT Data

☐ Calculate Over Only Interval:

Begin Index in Graph Time: 7

End Index in Graph Time: 1200

☑ Subdivide Graph Time Into Intervals

Number of Subintervals: 20

☑ Clear Previous Dilation Stress Data

Finished

Dilational stress calculations can only be made on movies where the drop volume is repetitively cycled by an automatic pump.

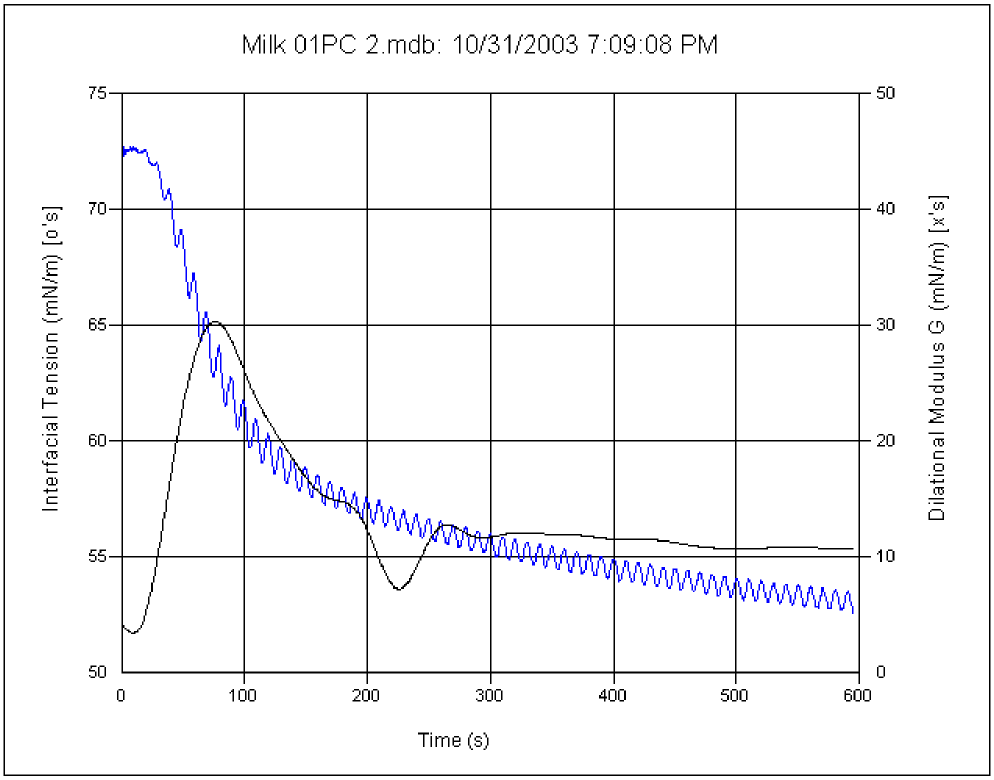
Calculation Results (click column to update FFT graphs)

Interval: Index Range	19: 1083-1151	20: 1143-1200
Dilational Modulus G	10.733	10.640
Modulus G Angle (deg)	8.6405	7.6818
Elastic Modulus G' (mN/m)	10.611	10.545
Loss Modulus G'(mN/m)	1.6125	1.4223
Elasticity n"(mN/m)	15.441	15.344
Viscosity n'(mN/m)	2.3463	2.0696
Differential Tension dIFT (mN/m)	0.4153	0.4008
Differential Area dA (mm2)	1.0649	1.0288
Mean Tension IFT (mN/m)	53.310	53.120
Mean Area A (mm2)	27.523	27.313
Fractional Area Change dA/A	3.869E-2	3.767E-2
Perturbation Period T (s)	9.1429	9.1429
Perturbation Frequency 1/T (Hz)	0.1094	0.1094

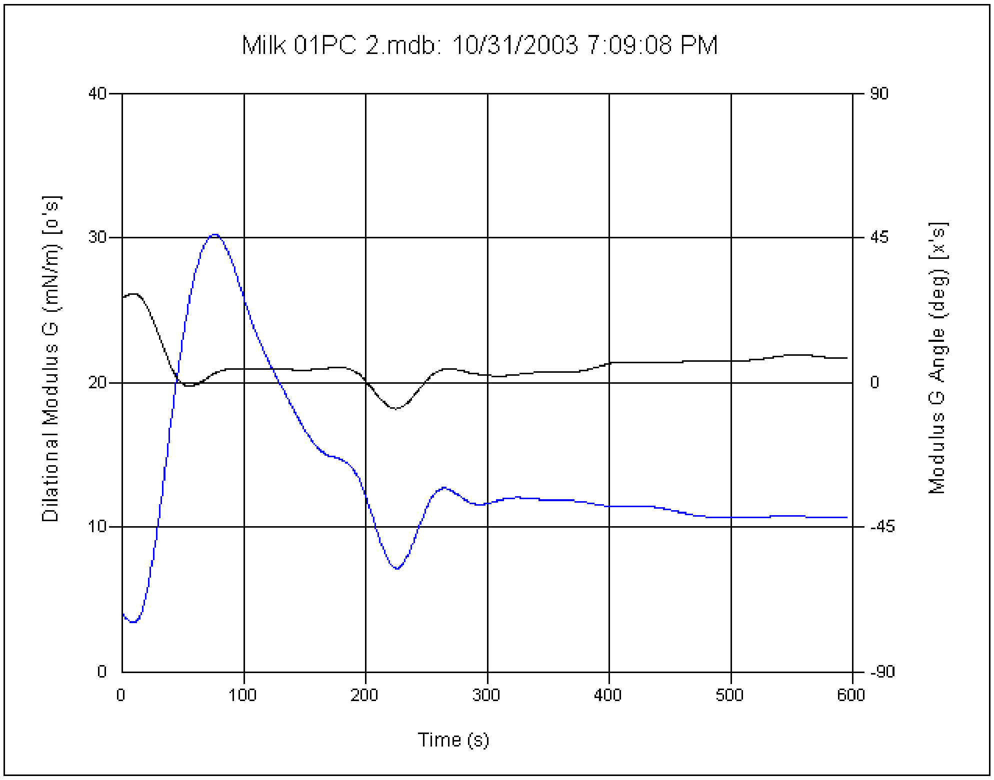
Final interval of run.

We now overlay the interesting dilational stress components on the interfacial tension graph. It will be seen the modulus starts low, at the beginning of the drop when the film has yet to form, grows to a maximum during the formation of the film, then settles back a bit after the film has formed.

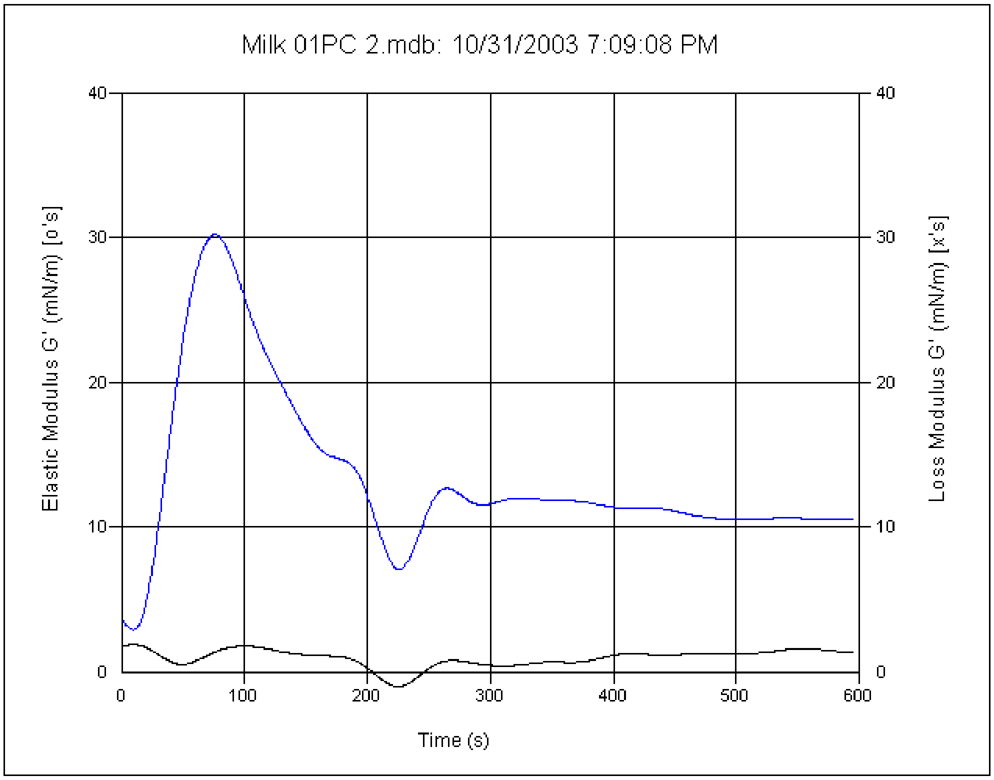
There is a small dip in the modulus at about 220s. The exact cause is not known but it may have been from the room heating/air conditioning system blower turning on. The images of the drop appear normal, but the interfacial tension does not respond to the area perturbation as much during this time. Remember each interval consists of only about three cycles, and the measurement is indeed sensitive, so any outside influence is important. A different run on the same sample does not show this extraneous dip. Graphs for this second run follow those of the first. Rather than discard the first run with the event at 220s, we chose to show it for its educational value [why just see perfect results?]. Since things happen during a run, someone bumps the bench or the air conditioning turns on, it is important to be able to recognize these for what they are. The overall features of the second run’s graphs are the same as the first. Note this second run was 500s long rather than the 600s of the other (this was a just matter of choice when the run was setup).



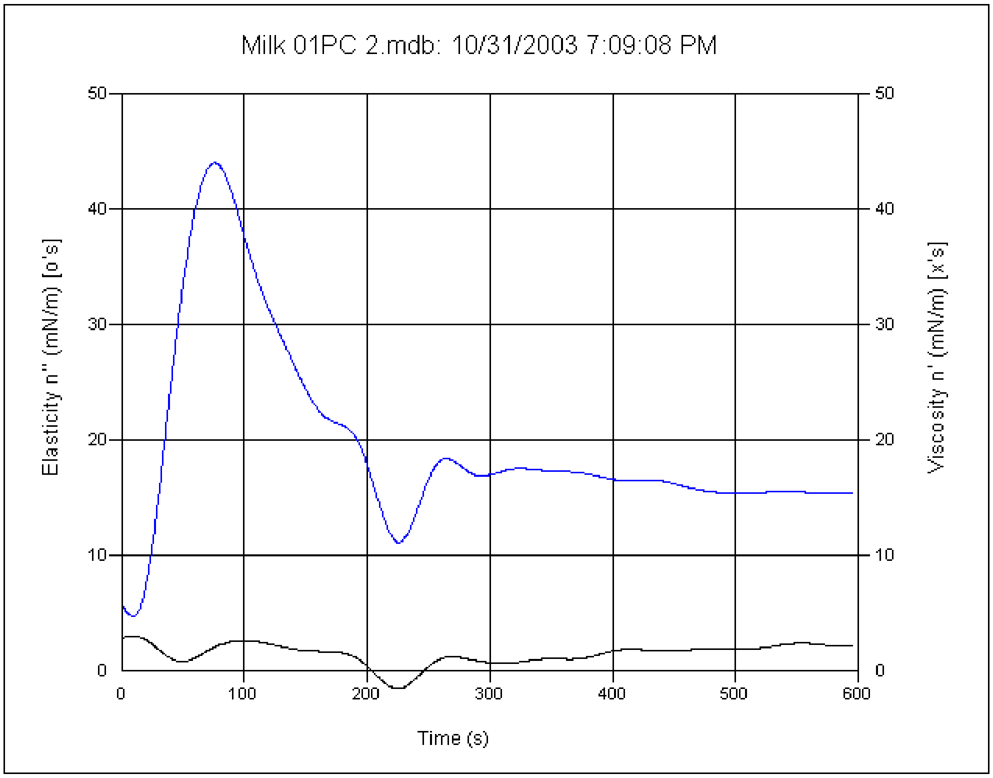
Interfacial tension and total dilation modulus G over run.



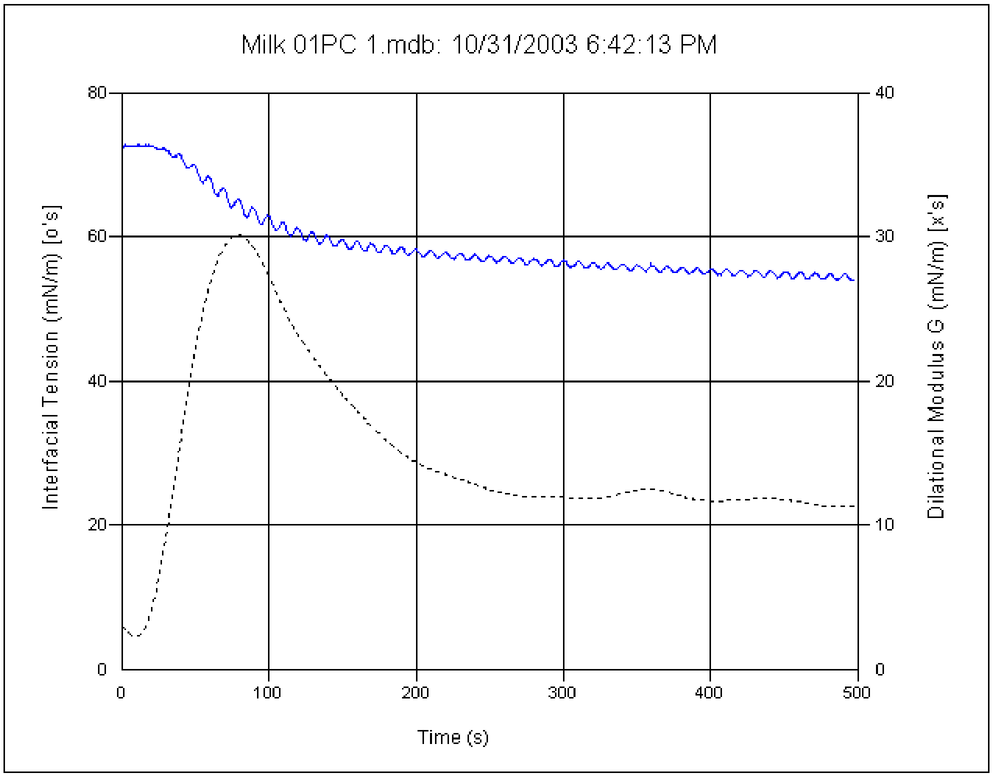
Modulus magnitude and angle; the angle plot is the center one that is almost flat.



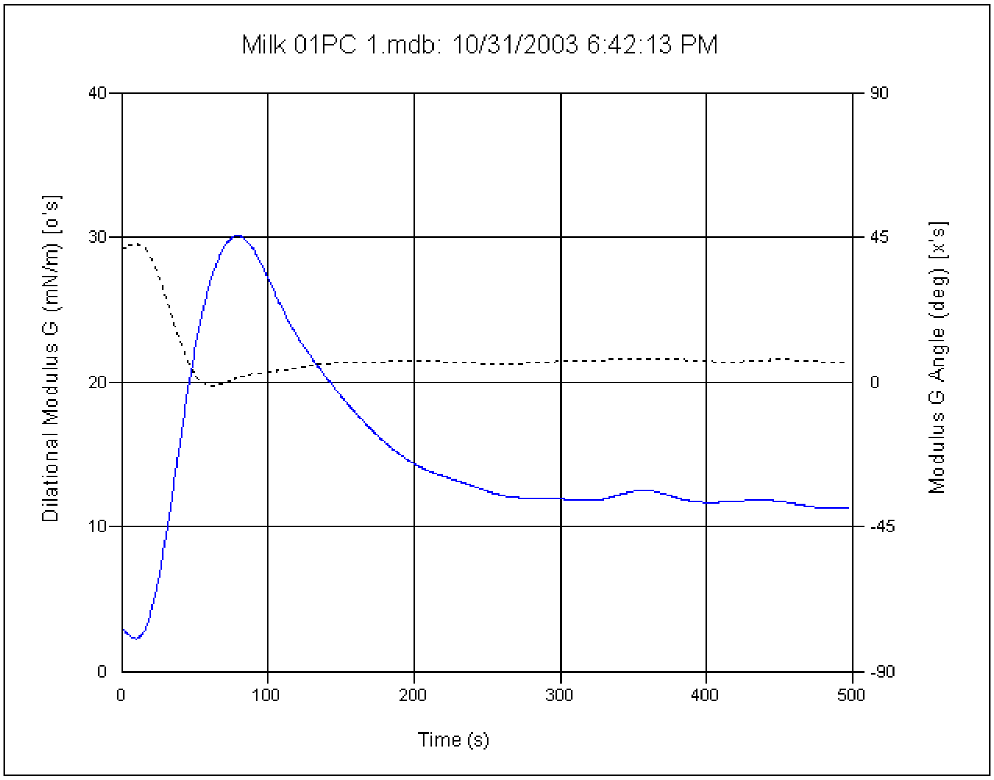
Elastic modulus and loss modulus, the latter being the almost flat curve at bottom.



Elasticity and viscosity; the film is primarily elastic; viscosity is lower, flat, curve.



Interfacial tension and dilational modulus for second run, with no event.



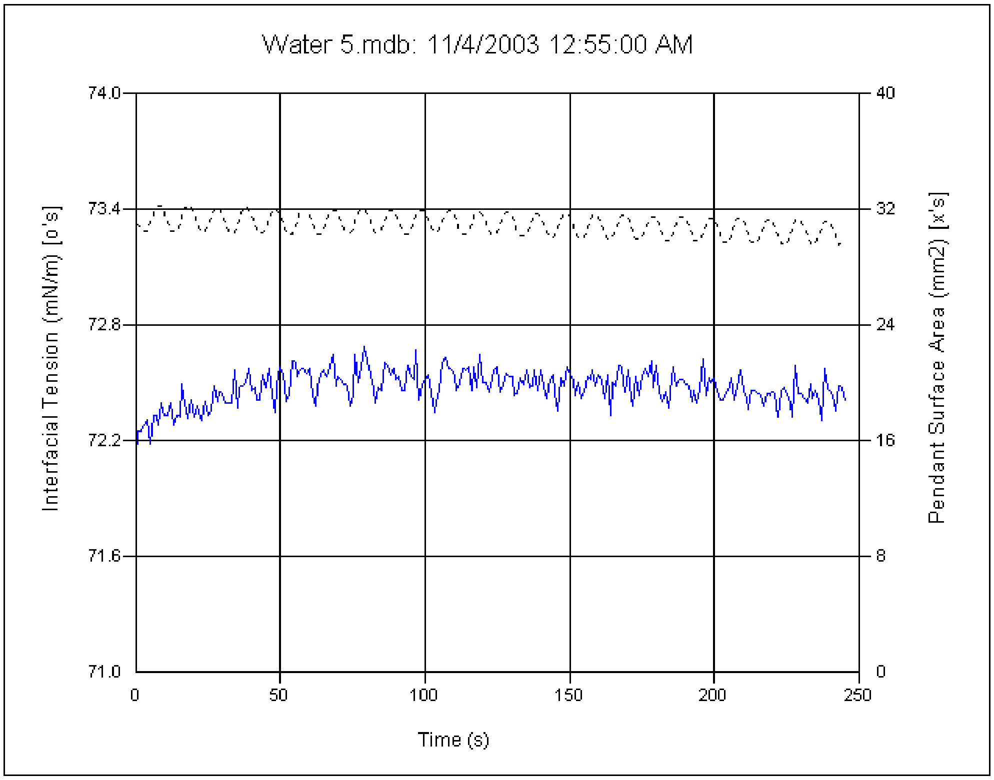
Modulus magnitude and angle; the angle plot is the center one that is almost flat.

Water as a Control

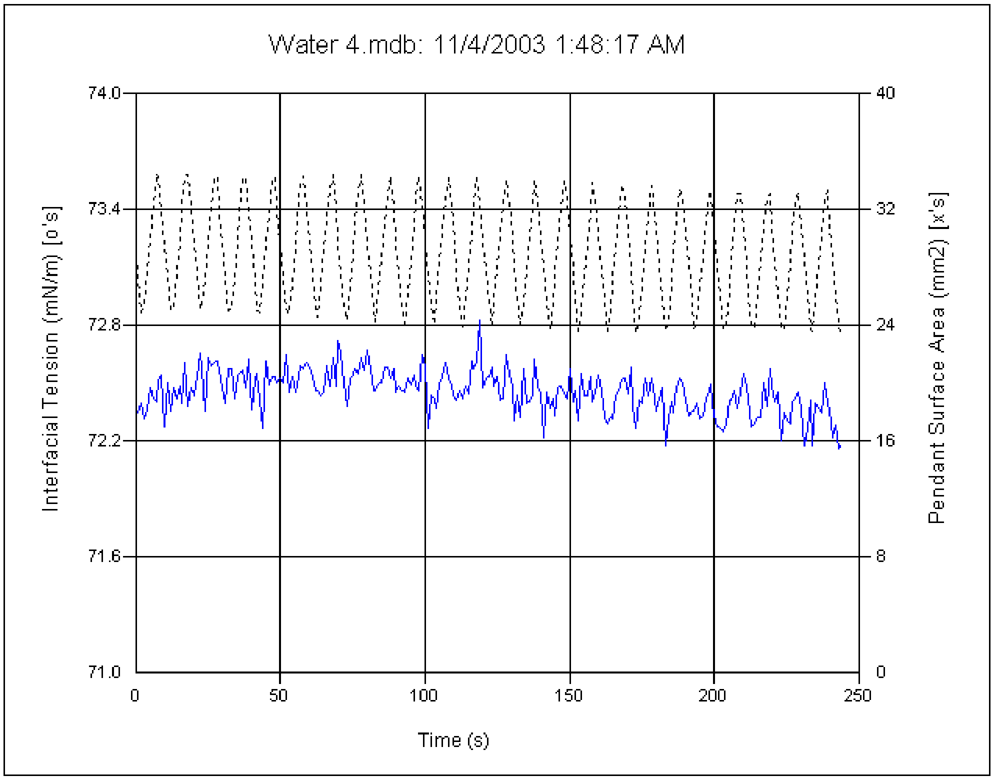
The dilution water was run as a control sample. Here we expect to find no dilational modulus (we assume it is zero). In truth, there are often very very small concentrations of contaminants that will show up in time. However, we will attribute all of the response we see in this experiment to instrument noise. This includes mechanical coupling of motion to the drop from the pump, electronic noise in the camera, and "sampling" noise from have a limited number of samples. In these runs, the perturbation period was still 10s but the sample rate was 1 image per second. Because we have a limited number of samples, variances which are not truly coherent with the perturbation will find their way into the transform peak corresponding to the perturbation. More samples, or a longer run, effectively average these out better. But we want to trace dilational stress changes with time, so we are limited anyway to samples of finite length in order to have time resolution in the dilational stress curves. Therefore the following graphs are representative of how you would use the instrument anyway (i.e., how you would actually use it, contrasted with the absolute *best* you could get).

Water was run with a small perturbation, 2.5% amplitude/5% peak-to-peak, and also a large amplitude, 13.8% amplitude/27.2% peak-to-peak. The drop was formed quickly and then perturbed at 0.1Hz for 250s.

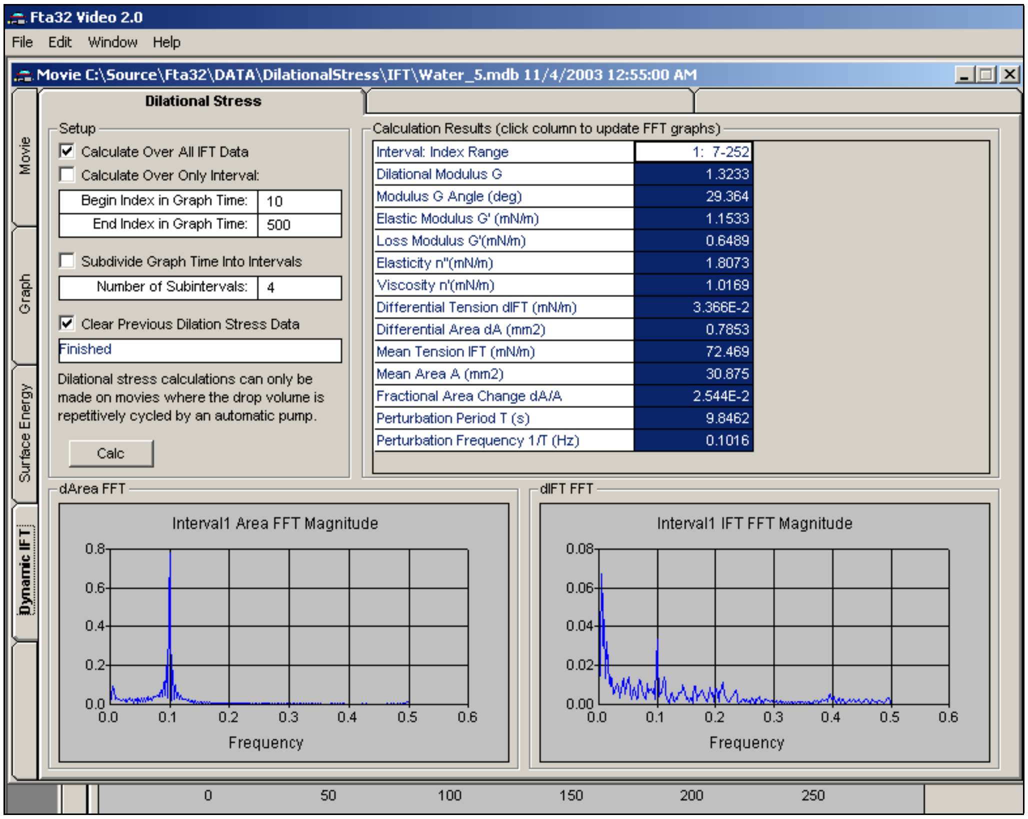
The first graph shows the small amplitude interfacial tension and surface area. As usual, there is no filtering applied to the data, although it is available within the analysis. These are raw data plots.



Interfacial tension and surface area with 2.5% perturbation.



Interfacial tension and surface area with 13% perturbation.



Movie C:\Source\Fta32\DATA\DilationalStress\IFT\Water_5.mdb 11/4/2003 12:55:00 AM

Setup

☑ Calculate Over All IFT Data

☐ Calculate Over Only Interval:

Begin Index in Graph Time: 10

End Index in Graph Time: 500

☐ Subdivide Graph Time Into Intervals

Number of Subintervals: 4

☑ Clear Previous Dilation Stress Data

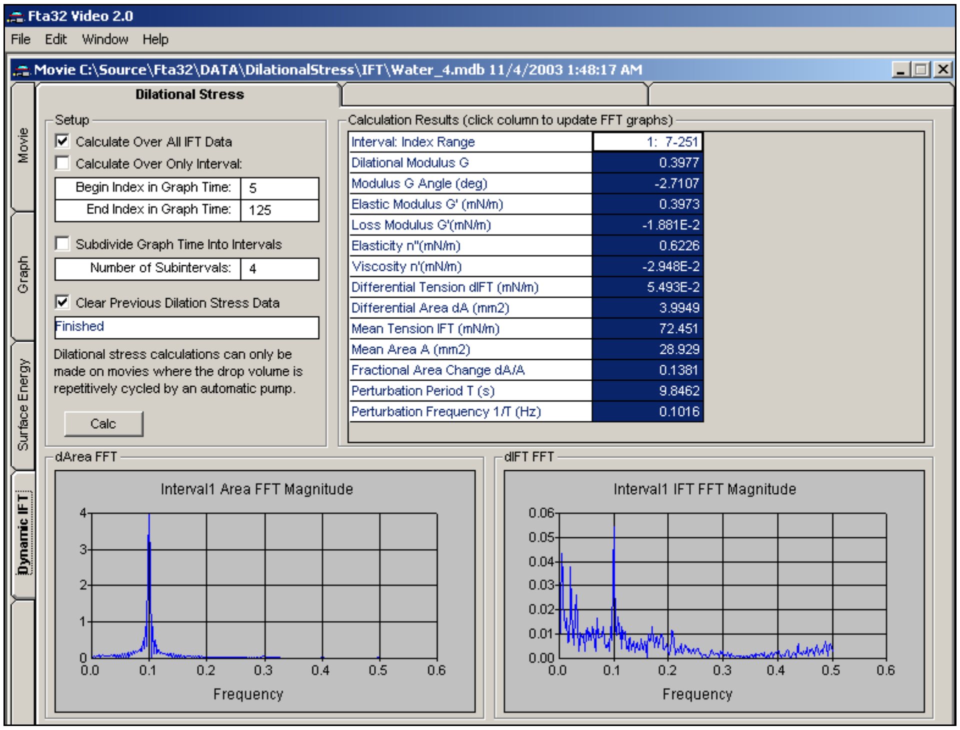
Finished

Dilational stress calculations can only be made on movies where the drop volume is repetitively cycled by an automatic pump.

Calculation Results (click column to update FFT graphs)

Interval: Index Range	1: 7-252
Dilational Modulus G	1.3233
Modulus G Angle (deg)	29.364
Elastic Modulus G' (mN/m)	1.1533
Loss Modulus G'(mN/m)	0.6489
Elasticity n"(mN/m)	1.8073
Viscosity n'(mN/m)	1.0169
Differential Tension dIFT (mN/m)	3.366E-2
Differential Area dA (mm2)	0.7853
Mean Tension IFT (mN/m)	72.469
Mean Area A (mm2)	30.875
Fractional Area Change dA/A	2.544E-2
Perturbation Period T (s)	9.8462
Perturbation Frequency 1/T (Hz)	0.1016

Fourier transforms for small perturbation of water.



Movie C:\Source\Fta32\DATA\DilationalStress\IFT\Water_4.mdb 11/4/2003 1:48:17 AM

Setup

☑ Calculate Over All IFT Data
☐ Calculate Over Only Interval:
Begin Index in Graph Time: 5
End Index in Graph Time: 125
☐ Subdivide Graph Time Into Intervals
Number of Subintervals: 4
☑ Clear Previous Dilation Stress Data
Finished

Dilational stress calculations can only be made on movies where the drop volume is repetitively cycled by an automatic pump.

Calculation Results (click column to update FFT graphs)

Interval: Index Range	1: 7-251
Dilational Modulus G	0.3977
Modulus G Angle (deg)	-2.7107
Elastic Modulus G' (mN/m)	0.3973
Loss Modulus G'(mN/m)	-1.881E-2
Elasticity n"(mN/m)	0.6226
Viscosity n'(mN/m)	-2.948E-2
Differential Tension dIFT (mN/m)	5.493E-2
Differential Area dA (mm2)	3.9949
Mean Tension IFT (mN/m)	72.451
Mean Area A (mm2)	28.929
Fractional Area Change dA/A	0.1381
Perturbation Period T (s)	9.8462
Perturbation Frequency 1/T (Hz)	0.1016

Fourier transforms for large perturbation of water.

You can see that the large perturbation case has slightly more noise in the interfacial tension plot. This comes both mechanical coupling of vibration into the drop and from the actual motion of the drop itself. When dispensing rapidly, the downward momentum of the drop results in a slight, artificial, decrease in apparent surface tension. The reverse happens on the upstroke and a higher tension is measured. These effects are on the order of 0.02mN/m when pumping rapidly. The pertinent results from these two runs are summarized in the following table. Note that peak-to-peak values would be twice the amplitudes shown.

Parameter	Small Amplitude	Large Amplitude
Amplitude of drop area sine wave (dA)	0.785 mm^2	3.99mm^2
Fractional change in area (dA/A)	2.5%	13.8%
Amplitude of interfacial tension sine wave	.034mN/m	.055mN/m
Dilational modulus G magnitude	1.322mN/m	0.398mN/m

These results show that, while the noise increases at higher perturbation amplitudes, it does not increase as fast as the fractional area change and therefore the overall uncertainty in the dilational modulus is less. An optimum value occurs at a fractional change of around 5% amplitude (10% peak-to-peak) as the interfacial tension noise increases little at first as the amplitude is increased. The peak modulus in the above milk results is about 30, so the implied coefficient of variance is

1.322 / 30 = 4.4%.

Again, higher perturbation amplitude would reduce this, but perhaps the film would be stretched beyond its linear limits.

Finally, the mean value of the two control plots is not absolutely constant. In particular, there is often a small rise in IFT during the minute after dispense, on the order of about 0.1 to 0.2mN/m. One hypothesis for this is temperature. This would correspond to a temperature change of about ½ -1 degree C. It may be that the glass syringe is slightly warmer than the environment (perhaps from handling or from motion of the pump) and that there is also some cooling effect as the drop evaporates. These are strictly guesses, but this variation does not affect the dilational stress calculations. It is just interesting.

Checklist for Dilational Stress Protocol

1. Syringe. A glass syringe, like the Hamilton, is a necessity. You can not use a plastic syringe for this work, although such are perfectly fine for contact angle dispenses. The optimum syringe volume is 250µl (but this work was done with 500µl). The plunger travels further, for a given displacement, in the 250µl syringe and this reduces the effects backlash in the pump mechanism. Furthermore, motor vibrations are at a higher frequency which reduces their effects on the pendant drop. Finally, the plunger has less friction in a 250µl syringe, and this too lowers noise.

2. Dispense Needle. Use a large needle. An 18GA needle is a good place to start. It has a nominal outside diameter of 1.27mm. Small needles do not support the pendant drop as well.

3. Filling the Syringe. Use a MicroFil 28GA non-metallic (fused silica) needle to fill the syringe from a second syringe. Hold the syringe to be filled (the 250µl one) upside down and fill from the plunger up. This prevents air bubbles.

4. Pump Mounting. The FTA200 pump has spring washers to allow it to be moved up and down. Tighten the mounting screws before running the experiment to prevent vibration.

5. Syringe Mounting. The FTA200 pump can accommodate different size syringes. Make sure the syringe body is grasped tightly; use the tension adjustment screws as necessary.

6. Cuvette. Use of a quartz cuvette to protect the pendant drop reduces the influence of air currents and you can control evaporation. This was not done in this work but is a good idea.

7. Air Table. If available, an air table protects against building vibration and accidental touching by persons in the room.

8. Sample Rate. Higher sample rates are better. More perturbation cycles are better. However these lead to long movies which are slow to load. Run short movies during

setup and inspect the analysis. Once you are satisfied, do not take a movie but simply make a DataLog which can be imported as an "imageless" movie and loads quickly. An alternative is to analyze the movie on-the-fly as it is acquired (turn on Live surface tension + pendant surface area measurements). Both of these options require the computer to be fast enough to analyze images without missing any. A reasonable computer can do 1 image per second and a good one about 4. Experiment by taking movies with Live measurements and see whether all images are already analyzed when you open the movie – any unanalyzed images indicate the computer missed one.

9. Perturbation Amplitude and Frequency. These are set in the Pump Program. What matters is the *stress rate* which is the amplitude divided by the cycle period. You can achieve the same rate by a small amplitude done quickly or a large amplitude done slowly. The latter is much preferred (will have lower measurement noise), as long as you have several cycles within each interval in your dilational stress calculation. In other words, if the physical phenomena changes within 5 seconds, you can not use a 10s period and expect to see the details — you need more like 1s.