Liquid-Liquid Interfacial Tension Measurements

October 18, 2006

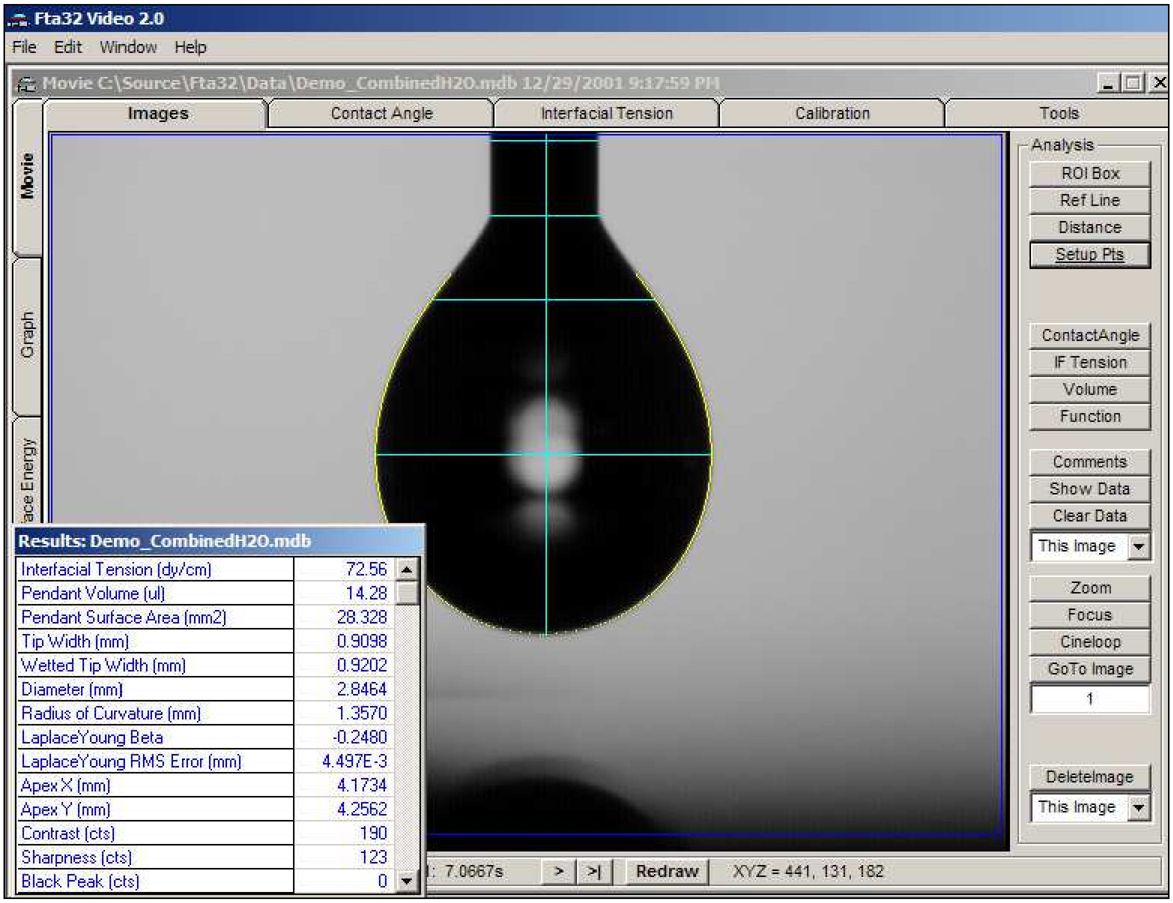
This note discusses liquid-liquid interfacial tension measurements on an oil-water system using an FTA200. In particular, it shows how to recognize certain difficulties in these measurements. A #20 "J" needle (0.914mm OD) introduced oil, the lighter phase, as a rising bubble into the surrounding water phase. Good IFT measurements require

- accurate magnification calibration (use the needle diameter if nothing else)
- sufficient distortion of the shape due to gravity: if the drop is tall enough, then gravity forces a change in pressure with height and the pressure change causes a change in radius of curvature. It is this change in curvature that we detect with the image analysis.

The reasons why provide an instructive lesson. First, let's look at a "normal" pendant drop used in liquid-vapor interfacial tension. It is *normal* for two reasons:

- it is hanging down. This means the drop is the heavy phase and the surrounding media is the light phase, referring to their densities. Normally we measure liquid-vapor tension and the vapor is the light density phase. However, we could *invert* the experiment and have a light bubble of vapor rising up from a needle in a sea of liquid. We would, of course, need a container (an *optically flat* container, that is) for the sea of liquid. An obvious case when this is useful is when you want to control humidity: you want to ensure the vapor is 100% saturated with the heavy phase vapor.
- it has a "pendant" shape. Pendant means gravity is pulling the drop's phase away from its support, say the needle. The other choice, sessile, means gravity is pulling the drop towards its support. Note pendant and sessile do not, by themselves, tell you whether the drop is hanging down or rising up.

The image on the next page shows the typical, normal, pendant shape hanging down. It has a liquid-vapor tension of 72.56, determined by Laplace-Young analysis. What we are interested in are two Laplace-Young coefficients: the "beta" (β) and the RMS error. Beta expresses the "roundness" or the "spherical-ness" of the shape. A perfect circle or sphere has a beta of 0. A negative beta means the shape is pulling away from the support, like this drop is hanging down away from the needle, but a positive beta means the drop is squatting down towards its support, like the ordinary sessile drop. The drop in the image has a beta of –0.248. This drop is clearly distorted by gravity. The drop typically falls off when beta gets near –0.3.

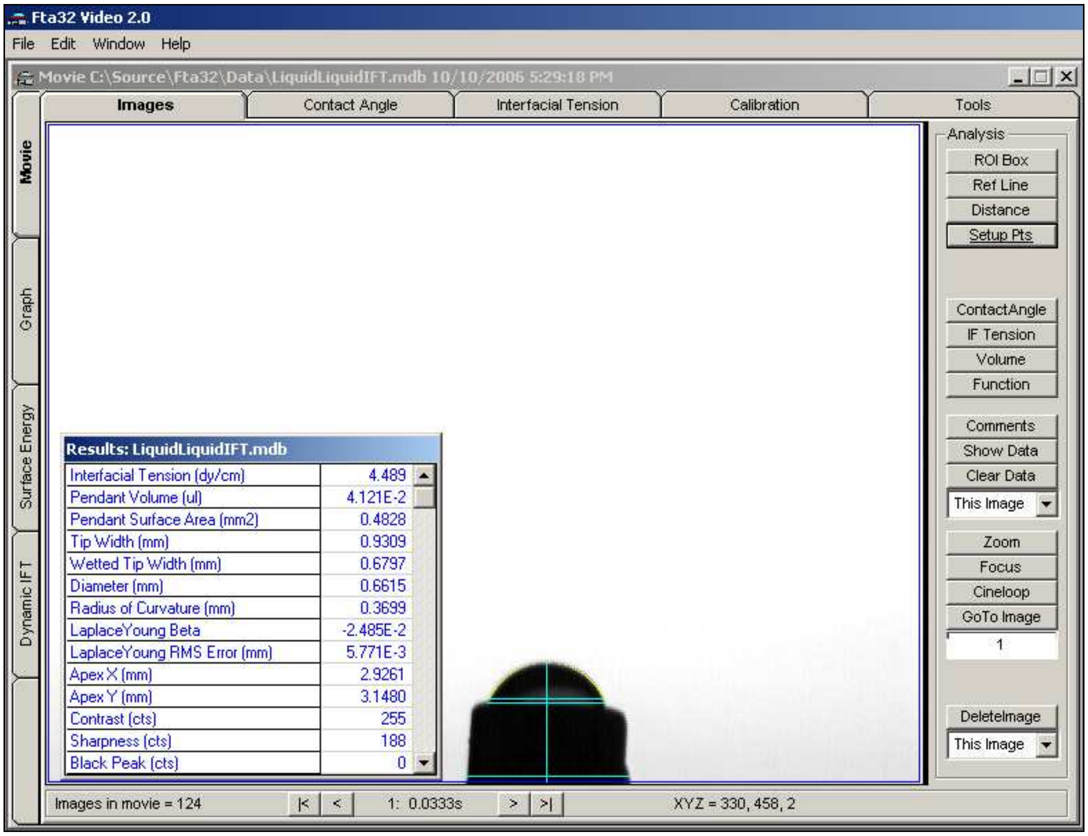


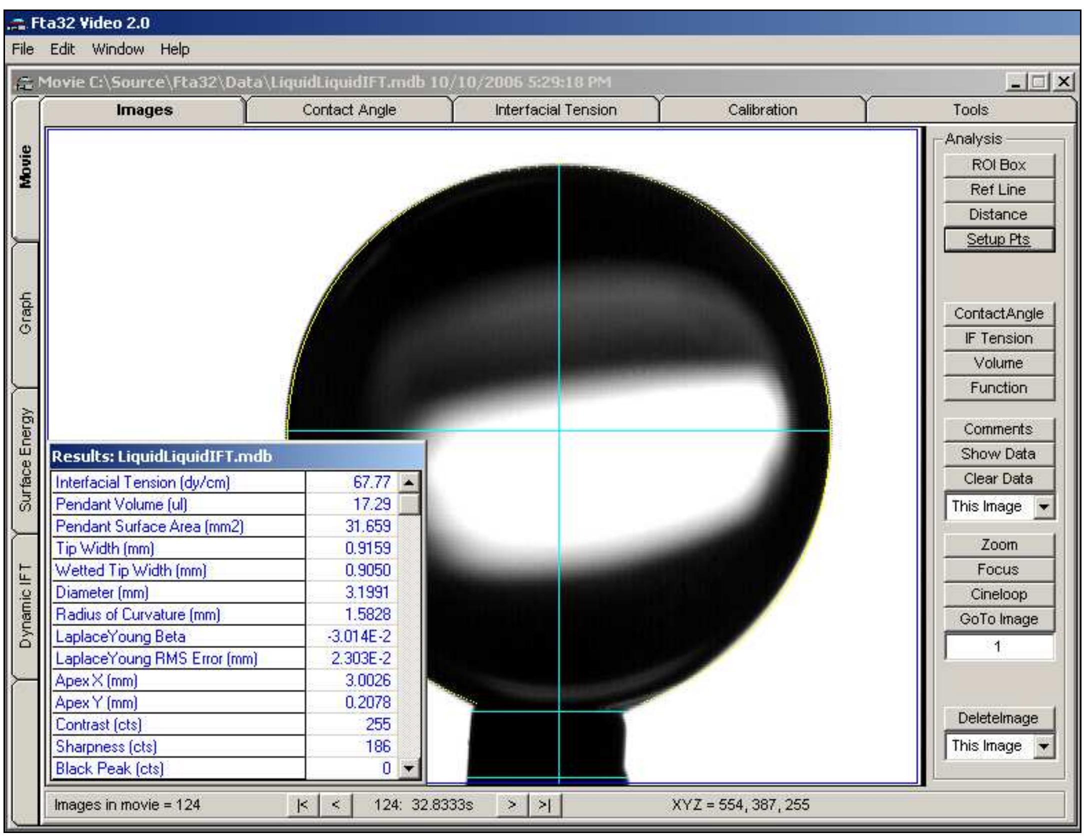
Normal pendant drop used in liquid-vapor surface tension. Beta and RMS error are in Results box.

The RMS error is the root-mean-square error of the actual edge location compared to the theoretical location of the drop profile for this beta. It expresses the quality of the fit of the ideal profile to the real drop. The above image has an error of 4.497 microns. We regard any error less than 10 microns as good and the result trustworthy. Larger errors signal something is wrong and the result is not trustworthy. Errors in FTA analysis typically run 2 to 8 microns.

Now let is look at the customer's Movie. He had a light phase of an oil and a heavy phase of water and he used a J needle to form an inverted pendant drop, a bubble. He started with very little of the oil phase showing at the needle tip and dispensed oil for about 30 seconds to form a fairly normal looking pendant bubble. The very first and last images of the Movie are shown on the following page. These give you an idea of the sizes and shapes of the bubble and the image quality. By the way, the image quality is excellent. That will not be the issue. The scale of the image is indicated by the needle diameter of 914 microns.

I do not know the actual liquid-liquid interfacial tension between this oil and water, but we can guess it is in the 50-60mN/m range. We will now look at the measured interfacial tension and the Laplace-Young coefficients as the bubble volume increased. You are warned that *all* the data we obtain from this Movie is suspect. That's what makes it such a fine teaching example.


Fta32 Video 2.0
File Edit Window Help
Movie C:\Source\Fta32\Data\LiquidLiquidIFT.mdb 10/10/2006 5:29:18 PM
Images
Contact Angle
Interfacial Tension
Calibration
Tools
Movie
Graph
Surface Energy
Dynamic IFT
Analysis
ROI Box
Ref Line
Distance
Setup Pts
ContactAngle
IF Tension
Volume
Function
Comments
Show Data
Clear Data
This Image
Zoom
Focus
Cineloop
GoTo Image
1
DeleteImage
This Image
Results: LiquidLiquidIFT.mdb
Interfacial Tension (dy/cm) 4.489
Pendant Volume (ul) 4.121E-2
Pendant Surface Area (mm2) 0.4828
Tip Width (mm) 0.9309
Wetted Tip Width (mm) 0.6797
Diameter (mm) 0.6615
Radius of Curvature (mm) 0.3699
LaplaceYoung Beta -2.485E-2
LaplaceYoung RMS Error (mm) 5.771E-3
Apex X (mm) 2.9261
Apex Y (mm) 3.1480
Contrast (cts) 255
Sharpness (cts) 188
Black Peak (cts) 0
Images in movie = 124
1: 0.0333s
XYZ = 330, 458, 2


Fta32 Video 2.0
File Edit Window Help
Movie C:\Source\Fta32\Data\LiquidLiquidIFT.mdb 10/10/2006 5:29:18 PM
Images
Contact Angle
Interfacial Tension
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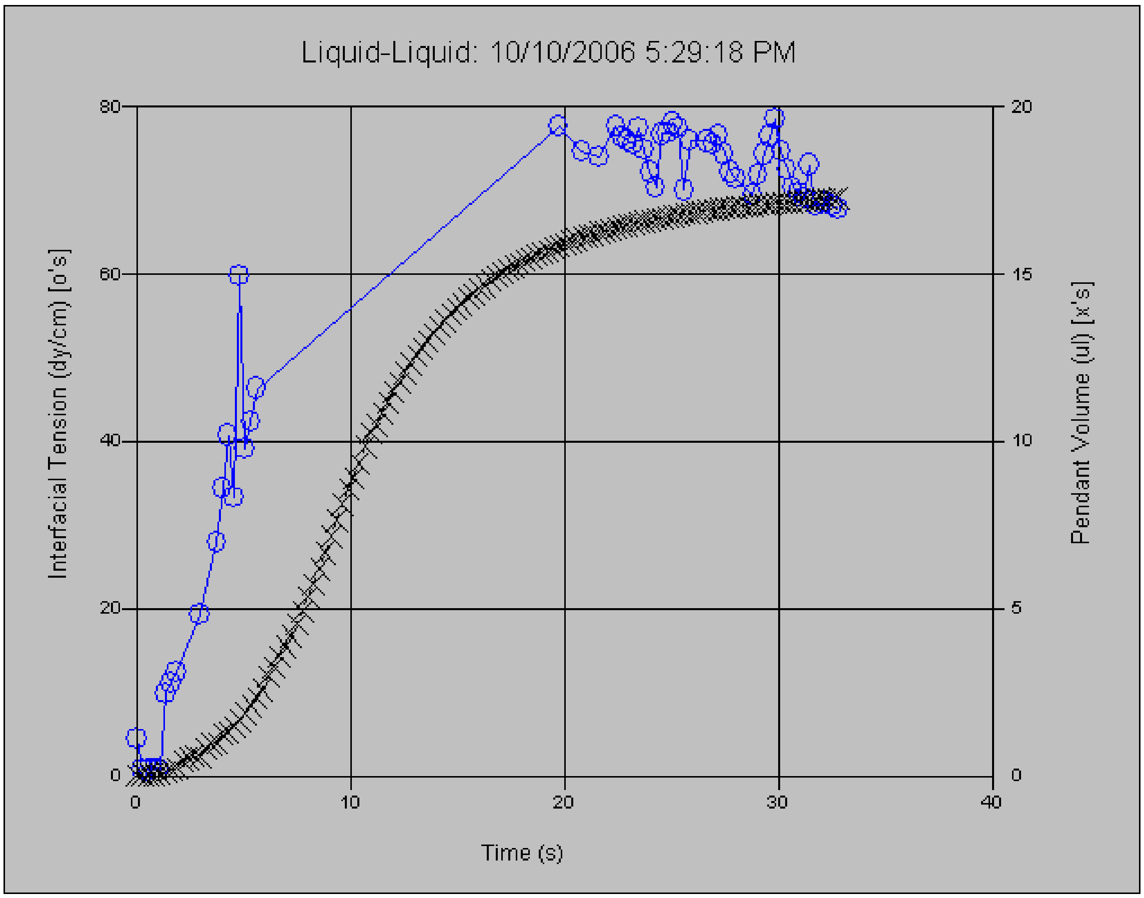
Dynamic IFT
Analysis
ROI Box
Ref Line
Distance
Setup Pts
ContactAngle
IF Tension
Volume
Function
Comments
Show Data
Clear Data
This Image
Zoom
Focus
Cineloop
GoTo Image
1
DeleteImage
This Image
Results: LiquidLiquidIFT.mdb
Interfacial Tension (dy/cm) 67.77
Pendant Volume (ul) 17.29
Pendant Surface Area (mm2) 31.659
Tip Width (mm) 0.9159
Wetted Tip Width (mm) 0.9050
Diameter (mm) 3.1991
Radius of Curvature (mm) 1.5828
LaplaceYoung Beta -3.014E-2
LaplaceYoung RMS Error (mm) 2.303E-2
Apex X (mm) 3.0026
Apex Y (mm) 0.2078
Contrast (cts) 255
Sharpness (cts) 186
Black Peak (cts) 0
Images in movie = 124
124: 32.8333s
XYZ = 554, 387, 255

What is so interesting is that the last image, at least, looks plausible for analysis. What is wrong?

First, we show the normal data output from such an experiment: interfacial tension and drop volume as a function of time. The circle points in the graph below are tension and the X points are volume. Tension is read on the scale to the left and volume on the right. While the volume increases smoothly from essentially zero to 17 microliters, the tension is scattered and missing many points. The missing points were rejected internally by the software as being inconsistent or clearly ridiculous. The plausible points vary from, again, essentially zero to about 80, but seem to be tending to something in the mid-60's at the end. How can the data be this bad? Well… in fact it is quite bad and alternative views will show that it is.

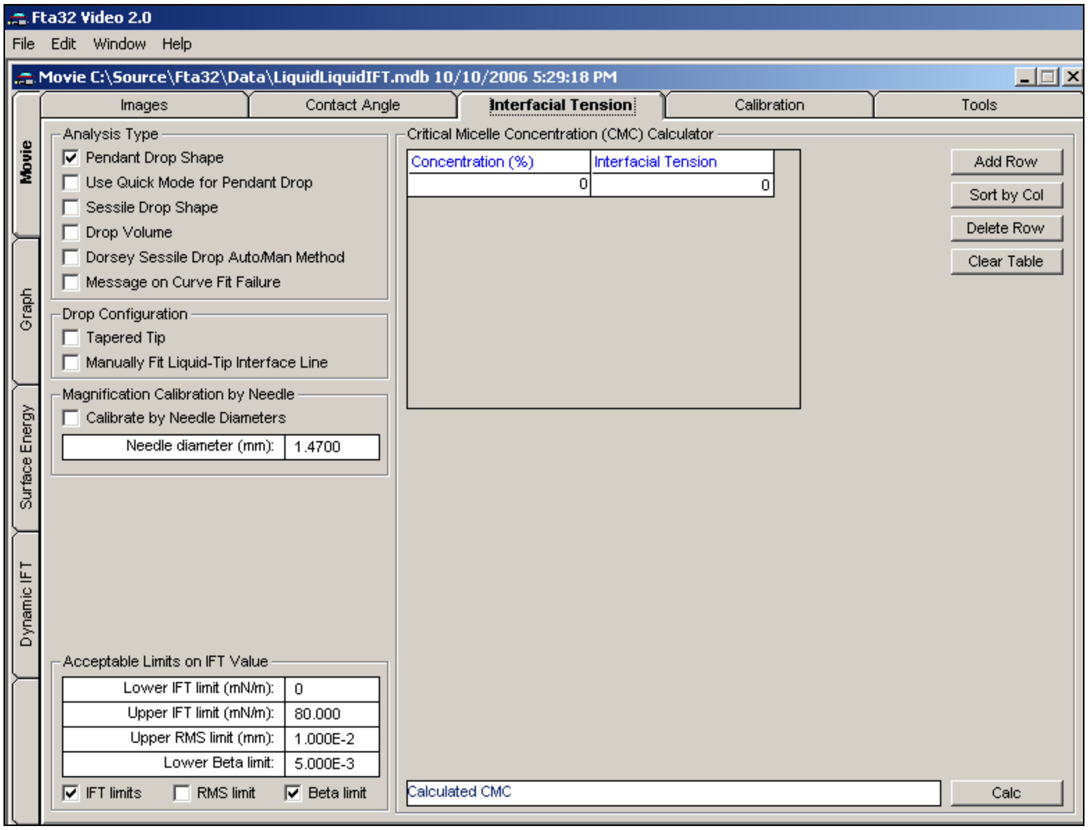


IFT (left, circles) and volume (right, crosses) over the 30 second oil drop dispense.

Basically we have two quality checks on the Laplace-Young answer:

- is the RMS error low?
- is beta reasonable?

The RMS error is the easier to apply, although one could argue the beta check is more profound. Both checks, plus limits on the acceptable tension, are available to the user on the Interfacial Tension tab, as shown on the next page.

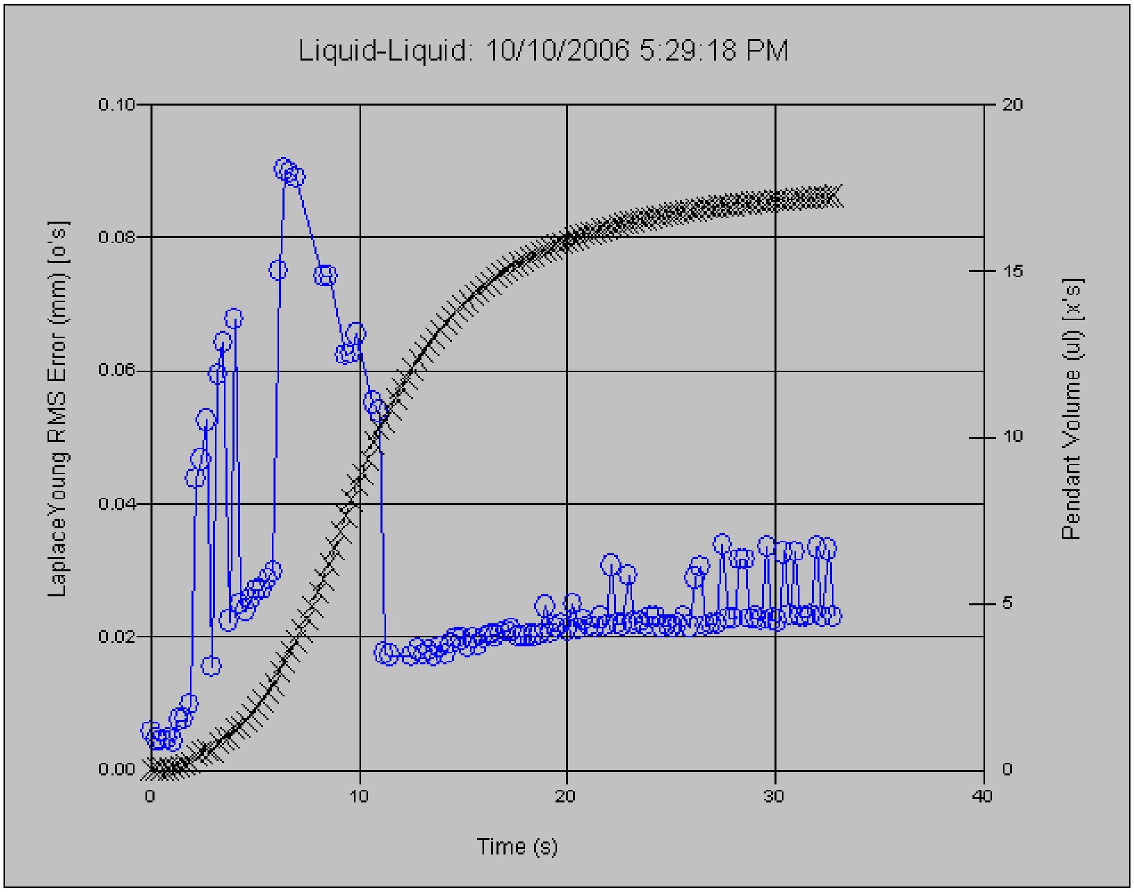


Limits for IFT upper and lower values, upper limit for RMS error, and lower limit for beta can be set and enabled on tab. IFT and beta limits are enabled in this example.

The graph on the next page shows the RMS error as a function of time, along with the drop volume to serve as a frame of reference. The error varies from something like 10 microns (0.01mm) at the very beginning, when the volume is essentially zero, to a peak of 90 microns and is over 20 microns for the entire second half of the run. We already know that gravity will not distort very small drops, so we can toss the very initial results without too much thought.

Notice that there are error points for every image – the error is reported even when the resulting interfacial tension is rejected because it exceeded one of the limits. That is why this graph has many circle points whereas the tension graph has considerably fewer. Irrespective of what limits the user sets, the software rejects tension data when the RMS error exceeds 30 microns. Recall 10 microns is what we think of with “normal” data, so this is 3×.

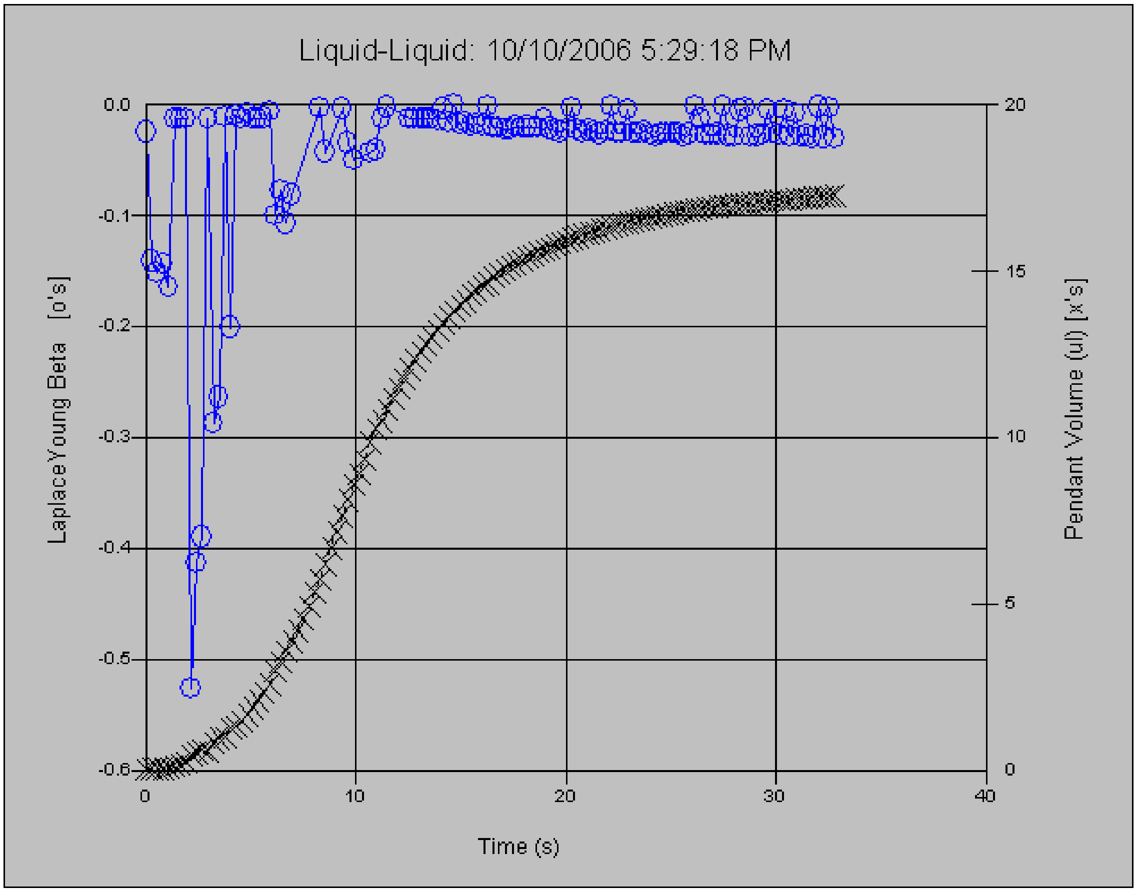
Since the RMS error is always above 20 microns, we can reject all tension data for this Movie. But why is the data bad? That requires more investigation.



RMS error as function of time. Volume shown as a reference for size of drop.

The next graph will show the shape factor beta during the run. We see beta is very scattered while the volume is negligible but settles down to something in the neighborhood of –0.03. Now what is an acceptable beta? Zero, recall, represents a perfect sphere, or circle in the 2-D image. We know that zero will not work because the distortion due to gravity is obviously zero and there is nothing for the Laplace-Young force balance to work against. The image on the first page had a beta of ≈-0.25. So we have a scale of 0 (bad) to –0.25 (good). My rule of thumb is that beta should be –0.1 or beyond. In fact, I normally set a limit of –0.15. These are arbitrary numbers, but they hint at the fact that –0.03 is not going to work.

The data in this Movie should be rejected on the basis of bad beta, if for no other reason. It is useful to know that the Laplace-Young equation *must* be solved numerically. There is no analytic solution. This means that the solution can converge to completely unreasonable numbers when beta is close to zero because small imperfections in the observed profile will send the solution to the far reaches of the universe. The tension numbers that were (automatically) rejected in this Movie were often in the neighborhood of 500 and some were above 1000. In a word, not close to 60 at all. As beta → 0, small image errors can cause *any* IFT to converge.



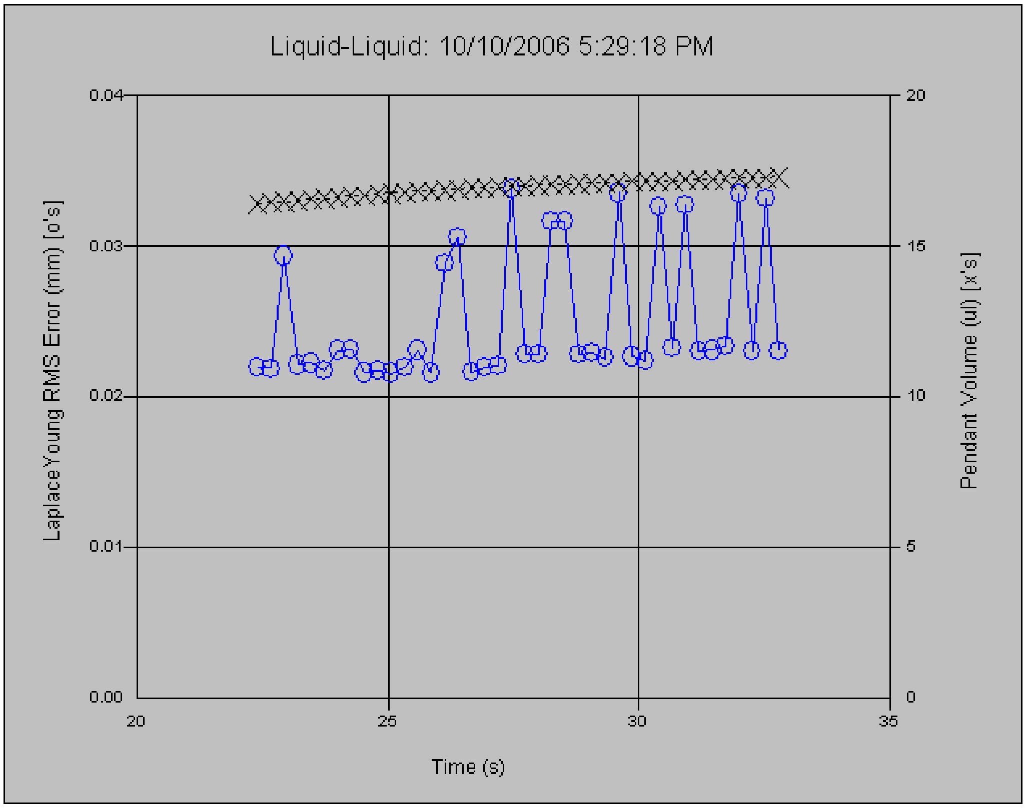
Beta (the shape coefficient) and volume.

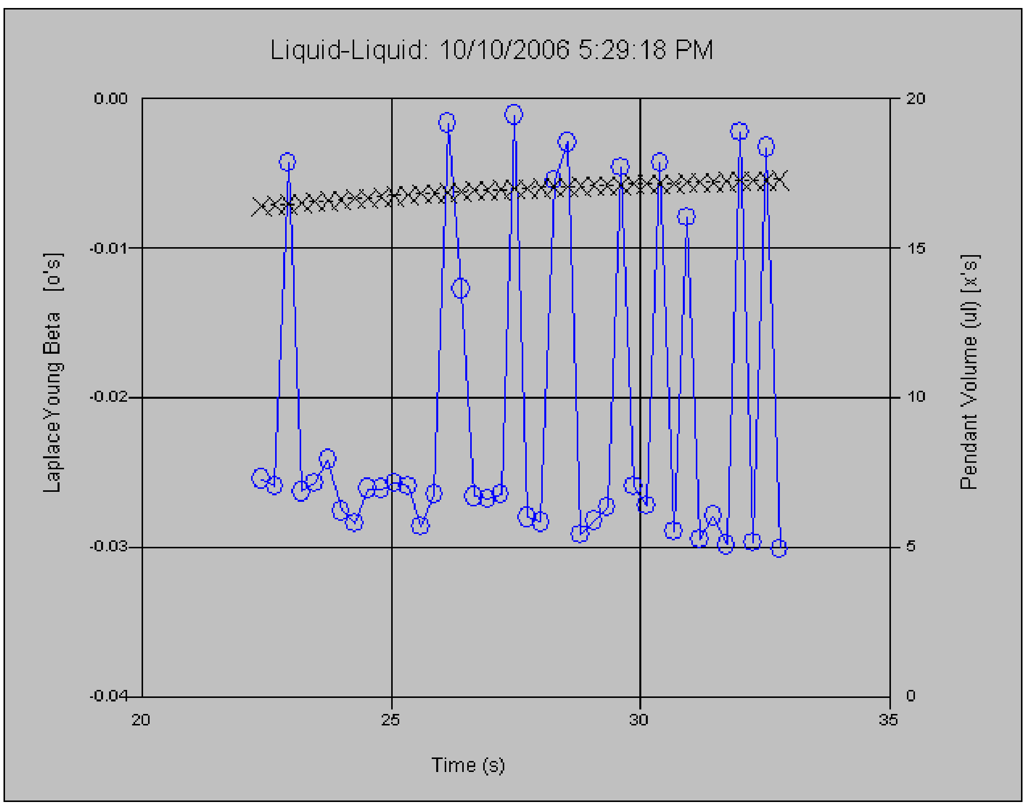
To reinforce these notions, the next three graphs are expansions of the previous ones and show only the final ten seconds or so of data, when the results have started to settle down and exhibit a trend. This restriction also allows us to rescale since the extreme scatter at the very beginning is excluded.

The RMS error plot shows the error bouncing between about 22 and 35 microns. Recall we automatically reject IFT solutions with errors greater than 30 microns, so the corresponding values were rejected irrespective of any further limits set by the user. Clearly this solution is in trouble.

The beta plot shows the shape factor bouncing between –0.027 and close to 0. This tells us the image shape is essentially a circle. The beta values are even more damming than the RMS error.

Finally, the third graph, on the subsequent page, shows a gradual trend in reported IFT down towards 65 and perhaps even lower. This hints at the correct answer as the drop comes within sight of the acceptable measurement region at the very end.


Liquid-Liquid: 10/10/2006 5:29:18 PM
LaplaceYoung RMS Error (mm) [o's]
Pendant Volume (ul) [x's]
Time (s)
0.04
0.03
0.02
0.01
0.00
20
15
10
5
0
20
25
30
35


Liquid-Liquid: 10/10/2006 5:29:18 PM
LaplaceYoung Beta [o's]
Pendant Volume (ul) [x's]
Time (s)
0.00
-0.01
-0.02
-0.03
-0.04
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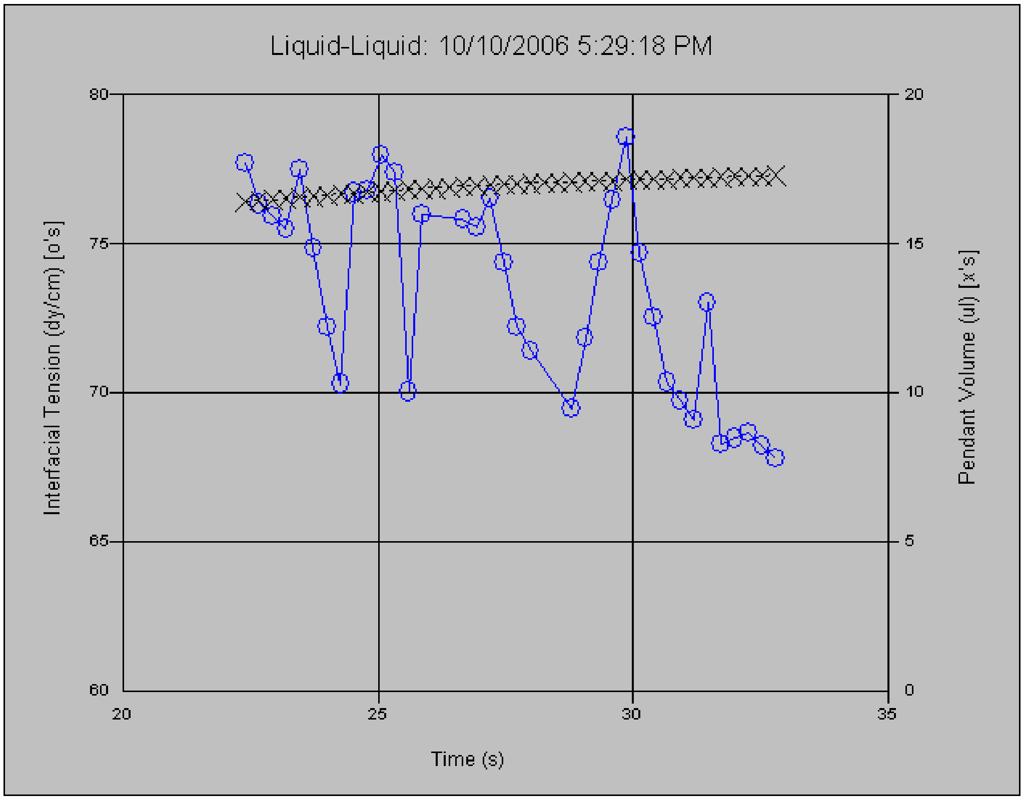
15
10
5
0
20
25
30
35



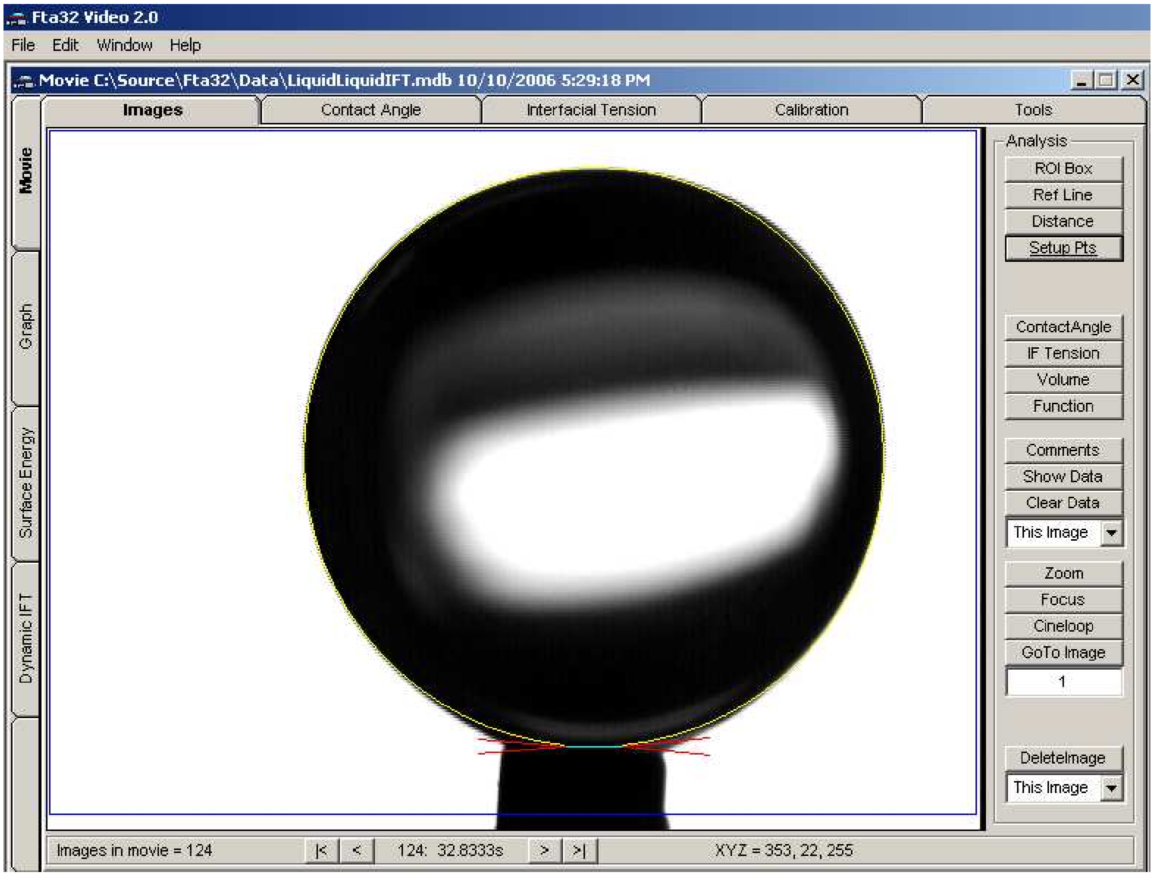
Three expanded graphs, two on the preceding page, showing RMS error, beta, and IFT at the end of the run.

OK, you say, you have proved the point that this data is suspect. Since the drops *looked* OK, why not just toss this technique as unreliable and use something else?

- first, we provide a method of determining the reliability of the measurement. In fact we provide *two* methods: RMS error and beta.

- second, and more importantly, pressure-based oscillating drop methods will suffer the same errors if the bubbles are not of correct size. The method that escapes is the maximum bubble pressure, but only because it consciously drives the volume until the bubble escapes and then looks back over the data to find the measurement point. Arguably you could do the same here: expand the bubble until it escapes. Perhaps the significant difference between the pressure-based and image-based instruments is that the pressure-based automatically drive the bubble to an acceptable size and the video-based measurement requires that the method be setup by the user to do so.

Finally, let's go back and look at the bubble image more closely and *see* where we got in trouble.



Last image in Movie, with spherical “contact angle” analysis
to draw a circle tangent to the bubble’s support on the needle.

We used the contact angle tool in an unusual way to draw a circle tangent to the needle tip. We care nothing about the reported contact angle and everything about the circle it drew.

- notice how the bubble is almost a perfect circle. This is why beta ≈ -0.03. The only deviation is down near the tip. Effectively the image analysis must determine everything from this deviation. Had we done the same thing on the normal hanging drop at the beginning of this note, the deviation is major and obvious.

- notice also the small excursion in the upper right corner of the bubble profile. When you watch the sequential images in the Movie, you can see the bubble moving back and forth and being slightly distorted as it does. This motion is the interaction of the disturbance in the vessel from expanding the drop and the viscosity of the liquid. This deviation, which moves in place from image to image in the Movie, affects the Laplace-Young solution. It competes with the deviation down at the tip. (Again, a bubble pressure instrument, with the same size bubble, would be similarly affected.) When the drop is distorted by gravity in the desired way, and hence beta ≈ -0.2, small disturbances such as this are swept away by the gross distortion of the shape by gravity.

Summary

1. Make sure magnification is calibrated. Magnification errors introduce a squared deviation in the reported tension.

2. Check the RMS error for a reasonable fit. Under most circumstances, an error greater than 10 microns should result in a rejected measurement. As a point of interest, 10 microns is the size of the average camera pixel, so this indicates the sensitivity of the instrument and its algorithms.

3. Check that beta is plausible. This is a method setup issue.

4. Do not depend on drop volume alone. The volume in this Movie was roughly 17 microliters. In an image like the liquid-vapor hanging drop at the beginning, this would be more than sufficient. But… and this is the point, it is the density *difference* between the light and heavy phases that determines the change in pressure from gravity, and therefore the change in radius of curvature $\rightarrow$ discernable interfacial tension. The density difference in this experiment is about 0.08g/cc. Roughly speaking, this scales the shape by a factor of 10 compared to a liquid-vapor setup where the density of the liquid might be 0.8g/cc. This means our 17 microliters is more like 1.7 microliters in an ordinary setup. (To be precise, what matters is the density difference $\times$ the drop height, so the above is a very rough approximation.)

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