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A PROGRAM SYSTEM FOR INTERFACIAL TENSION AND CONTACT ANGLE MEASUREMENTS BY IMAGE ANALYSIS

Advanced Edition

By

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Manual Edition 1.4

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INTRODUCTION

Interfacial and surface tension of liquids are of importance to many processes in the chemical industry. There is a need for a fast and easy technique with satisfactory accuracy and reproducibility. Traditionally, instruments utilizing the Du Noüy ring and Wilhelmy plate methods are utilized throughout the industry and research laboratories. The methods of pendant or sessile drop are traditionally well suited for many types of surface and interfacial tension measurements, but are also quite time consuming. Drop shape analysis has usually been performed by photographing a drop in an optical bench arrangement, and then the characteristic sizes of the drop can be measured on the photographic prints. For pendant drops the maximum diameter and the ratio between this parameter and the diameter at the distance of the maximum diameter from the drop apex has been used to evaluate the size and shape parameters (1), whereas for sessile drops a complete profile matching is often necessary. After video imaging facilities and mathematical coprocessors for personal computers have become readily available, there is a great potential for improvement of this method.

On the basis of the Young-Laplace equation describing the drop profile of both sessile, pendant and ascending drops and bubbles, it is possible to calculate the surface tension from digitized picture data (2-3). Much attention in the scientific community has been focused on sophisticated numerical methods for image analysis and integration. Although these methods sometimes may produce excellent results, they are often too computation intensive to be applicable in everyday instrumentation, although the speed of these computational algorithms have been greatly increased since the introduction. The objective of this program has been to construct a simple and fast instrument with sufficient accuracy and reproducibility to make this method useful in many practical applications. This manual describes a computer program that utilizes pictures taken with video and frame grabber equipment and an IBM compatible PC. The general physical and mathematical properties of this method are published, and are also outlined in Appendix 1.

PROGRAM FEATURES

The DROPimage Advanced program has a number of features that make the procedure of surface tension and contact angle measurements easy and versatile. The type of measurement, number and timing, calibration, data presentation and analysis are all controllable within the program, and the exchange of data with other program by standard Windows procedures make further presentation and analysis convenient.

The main measurement capabilities are the following

Type of drops

- Pendant
- Inverted Pendant
- Sessile
- Captive Bubble

Type of results

- Surface/interfacial tension
- Contact angle
- Surface energy of solids
- Drop dimensions, such as
  - Height
  - Width
  - Radius of curvature
  - Volume
  - Surface area
- Surface elasticity and viscosity

Type of measurements

- Constant volume drops
- Volume steps and relaxation
- Oscillation

ON-SCREEN AND REAL-TIME IMAGE DISPLAY

The main window contains he captured image. This picture is scalable and is used to set the limits and start position for the edge detection algorithm. The detected

edge is also plotted in this picture as a visual indication of the correct operation of the edge detection. In addition to this picture, a real-time (passthru) display of the camera output is also available, either in a 1:1 or a 1:2 scale. The real-time display may be switched on and off by using the Start passthru/Stop passthru toggle on the View menu. The real-time display always starts in a 1:2 scale. By double-clicking the window, the scale is changed to 1:1 and back again.

TABULAR DISPLAY OF ALL RESULTS

All results are displayed in tabular form in the program's **Results** window. This window contains two tabbed notebooks, one for surface tension measurements and one for separate (contrary to those included with surface tension results) contact angles. These results may also be displayed in a separate **Report** window that is specially formatted for printing. For visual display, the program contains a **Plotting** function.

METHOD DRIVEN MEASUREMENTS

All measurements of surface tension and contact angle are based on measurement **Methods** (except measurements with the Contact Angle tool). A method consists of a collection of parameters that describes how and when measurements are performed and how results are saved and presented.

A method's parameters are saved in a text file. Methods are created and edited in the **Method Editor**. All measurements of interfacial tensions must refer to a method, and several measurements can use the same method.

There are principally two kinds of methods, depending on the first field, Data source. If this is set to Video, data are taken from the frame grabber board for further treatment according to the other parameters. If Data source is Disk file then this is a **Recalculation** method that tells the program to read data from a disk file, which must have been produced by a method where the data source is Video. For further description of the method parameters and editor, see the Method Editor section.

MEASUREMENT PARAMETERS

In order to calculate surface tensions, the program must know the densities of the two phases and the picture magnification. These data are saved in a **Parameter File**. The parameters are created and edited in the **Parameter Editor**. This editor is connected to the **Phases data file** that contains the density data of many popular liquids and gases. This data file is maintained in a separate **Phase**

Editor. In addition to the input parameters in the Parameter editor, two parameters are automatically added from the calibration values. By means of the measurement parameters, surface tension can be measured by a simple procedure leading to a single or multiple readings according to the method in the parameter file.

NEW EXPERIMENT WIZARD

In order to make the setup of a new experiment easy, the program contains a New Experiment Wizard that will produce method and parameter files on the basis of input prompted from the user. The wizard may be set to launch automatically when DROPimage is started. The new files are produced in standard format and may be freely tailored afterwards, if desired.

INTERRUPTIBLE MEASUREMENTS

A mayor advantage with the present Windows program is that the measurements are interruptible. This means two things:

1. During measurements, the other windows programs may run at the same time. The DROPimage program sees to that measurements are taken at the predetermined times. As long as the Passthru image is not displayed, the program does not take many resources from the operating system.
2. The measurements may be stopped at any time by means of the abort button in the measurement status window. An aborted measurement may be continued later.

An exception to the above is when measurements are taken real-time, at the maximum rate. The program then will lock out other processes in order to perform the task as fast as possible.

CALIBRATION

Because the optical magnification may be changed and adjusted by the goniometer and lens system, calibration of the total magnification in the system is needed whenever the magnification is changed. Accurate calibration is also of paramount importance to obtain reliable readings, because the error in surface tension is twice that in the magnification. Because of this, calibrating the magnification has been made an integrated part of the program. Calibration is performed by measuring a cylindrical or spherical object that has been accurately measured by other methods. By using the same data treatment techniques as in

the drop profile detection, the optical and mathematical errors are minimized, given the diameter of the calibration object is comparable to that of the drop.

In the calibration routines, it is also possible to adjust the horizontal/vertical aspect ratio. This value is a fixed number for a given camera/frame grabber combination, and would ideally be a universal constant because of standardized video camera construction. However, different cameras may have slightly different aspect ratios, this may therefore conveniently be adjusted either by calibration both in vertical and horizontal direction, and by using a sphere for calibration.

CONTACT ANGLE MEASUREMENTS

Usually the goniometer may be used both for the analysis of drop shape, size and contact angles. As the latter does not need any calibration of magnification (except for the aspect ratio), this is usually much easier than surface tension measurements. In a manual goniometer, contact angles are measured by means of a graduated scale and a cross hair in the optical reticule. This program implements several methods to calculate contact angles by means of image analysis of a drop.

When surface tension is calculated (by the Contour or Optimized methods), the contact angle is always calculated from the theoretical profile. This method is considered quite accurate, but requires that the whole drop is visible and that the drop profile is undisturbed. The method also will only calculate an average of both sides because the theoretical profile is always symmetric.

The program also implements methods to calculate the contact angle of each side of the drop independently, by pure geometric means. These methods are the same as used in the DROPimage Standard program. The methods are: Circular curve fit, secant extrapolation and linear fit. Because only a part of the drop is used, measurements of advancing and receding contact angles by means of the pipette method are easy. Either one or both sides of the drop may be measured separately, and in the latter case the average and difference are also calculated.

The contact angle results may be saved as contact angle files that are used in the **solid surface energy tools**.

SURFACE ENERGY TOOLS

DROPimage contains a collection of tools for the calculation of surface energy of solids form contact angles. These tools have the same functionality as the RH Imaging 2001 Tools, but have enhanced error calculation. There is also an additional tool for the calculation of the surface energy of high-energy solids by

measuring contact angles of one liquid in another (solid/liquid/liquid). Contact angle (CA) files are interchangeable between RHI 2001 and DROPimage.

DROP DIMENSIONS

The height and width of the drop are calculated from the experimental profile. As a part of the interfacial tension measurements, the program performs a numerical integration of the drop profile to determine the volume and surface area. This opens several possibilities for additional and complementary use of the program. The volume data may for instance be used to calculate mass transfer rates (evaporation, dissolution etc.). In addition the system contains a feedback drop volume control where the computer-controlled auto syringe may be used to keep the drop volume constant. This has great advantages in experiments that are very sensitive to area changes, such as for instance polymer adsorption that also usually take long time (hours/days). The measurement of surface area makes it possible to calculate area/surface pressure curves and to look at surface tension relaxation and surface dilatational elasticity and viscosity by means of oscillation measurements.

DATA EXCHANGE WITH OTHER PROGRAMS

Both raw images and processed data in several forms may be exported to other programs, both through the Windows clipboard and different data files. Video pictures may be captured and copied to the clipboard or saved to disk outside the method controlled measurement procedures. The pictures may also be loaded from or converted to other bitmap file formats such as the standard Windows bitmap format, BMP, GIF, and TIF. This makes it possible to export pictures to other applications. After edge detection ("filtering") the profile coordinates may be saved as a binary or a text file, ready to be read by other programs. In the main result table, copying to the Windows clipboard is also supported.

The results from the calculations may be saved and exported to other programs. All results are saved to **LOG-files** on a per experiment basis. Through a Session control window the log-files may be viewed plotted and edited. The log-files are ordinary text-files that are easily read by other programs.

The program also has a Report facility that produces a **rich text formatted** (RTF) report that can be readily read into word processing programs. The experimental data that go into the report may be selected among the available results, and the report window has editing and formatting properties that makes it a small text editor. The reports may be saved and printed form the Report editor.

Results form contact angle measurements may be stored in special **contact angle files** (*.CA) that are used in the surface energy tools. These files are compatible with the Rame-Hart Imaging 2001 software tools and contact angle data may thus be shared between these and DROPimage.

The program has additional procedures and options in order to make "house keeping" tasks easier and also makes detailed control of picture taking, edge detection, data storage and retrieval possible.

An additional function on the View menu is the "Intensity histogram". This generates an intensity map along a number of either horizontal or vertical pixels and is especially suited to study the intensity level and change across the profile for instrument adjustment and/or error investigation.

ONLINE HELP

The program has a built-in help Windows system that contains much of the same information as this manual. The help system is accessed by the Help menu, by pressing F1, and by Help buttons in many dialog boxes.

USER'S GUIDE

Below is given a detailed description of the user interface with menu options and measurement procedures.

STARTING DROPIMAGE

The DROPimage program may be started from the shortcut on the Start menu in the RameHart group or on the Desktop, or directly by double-clicking the Dropimg.exe file. The program will detect and initialize the frame grabber board, and therefore cannot be loaded simultaneously with other programs using the frame grabber (for instance the DROPimage Standard program). If loading of the DROPimage program is attempted at the same time as another program is using the frame grabber, the frame grabber cannot be initialized. If this happens, the other program must be closed before attempting to start DROPimage again.

HOW TO EXIT

You exit DROPimage by selecting File | Exit from the main menu or by pressing the x in the window's upper right corner.

SELECTING FUNCTIONS

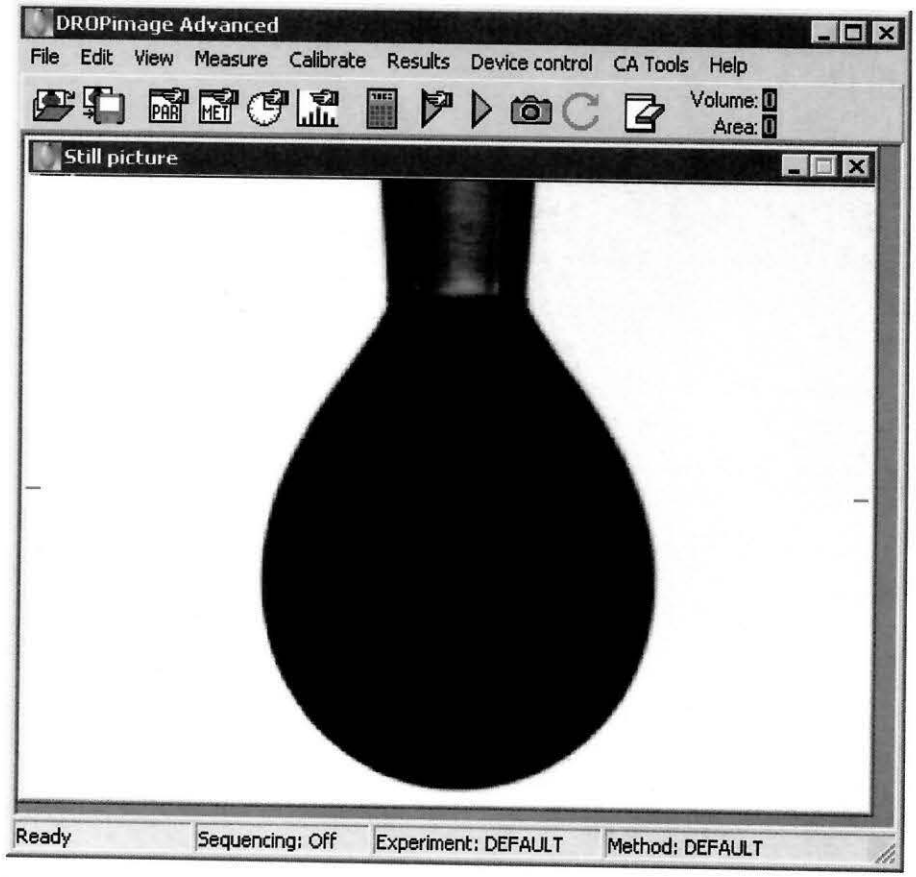
The program is controlled from the main pull down menus. For some of the main functions such as loading and saving pictures, editing parameters, methods and time files, starting an experiment and erasing the result screen, speed buttons have been provided.

In the **editor screens** the cursor may be moved either by means of the tab key or by pointing and clicking with the mouse. <Esc> is pressed during an edit session, the window is closed and the old values will be kept unchanged.

THE MAIN WINDOW

The Main Window is shown below and contains the main menu bar, the speed buttons panel, the surface area and volume display, the captured "working image", and a status line at bottom. The status line contains the Message field, the Sequencing on/off status field, the active method field, and the active parameter file field.

Main Window with the Main menu, the captured picture and the Status line

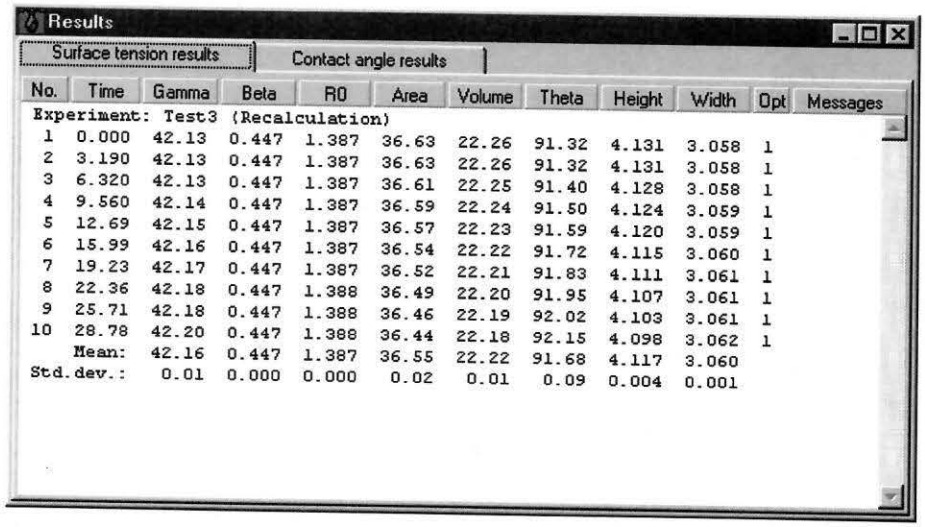


The Volume and Area display fields on the right side in the speed buttons panel continuously show the drop's volume and area **during a measurement**. The fields are updated at regular intervals that are determined by the value of the Timing interval for volume control box in the Options window. The default is 5 seconds. You cannot maximize or close the Picture inside the Main window, and the window can only contain one picture at a time. **NOTE: You should not maximize the Main window (so it fills the whole screen). If you do, some of the dialog windows may fall outside the screen or behind the Main window, and become invisible (!)**

RESULTS AND THE RESULTS WINDOW

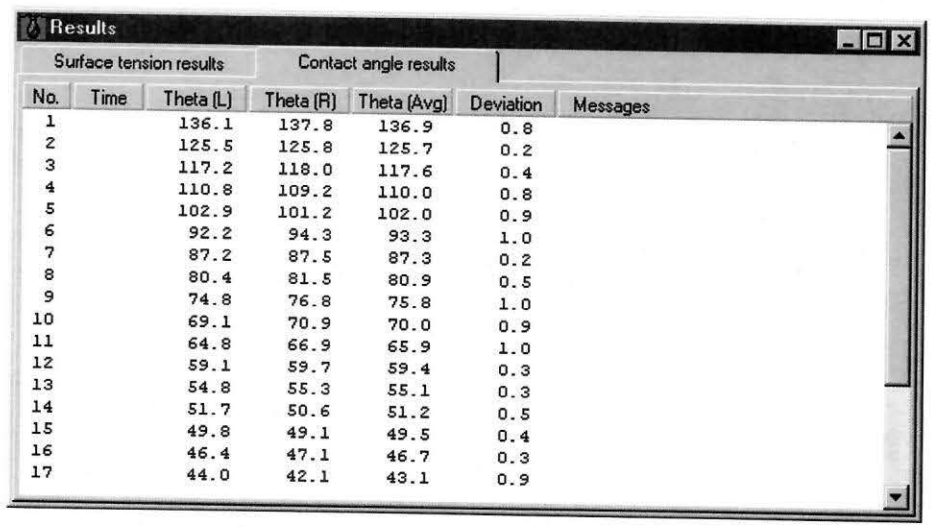
The results are displayed in the **Results window** that contains two tabbed notebook pages, displaying the results from surface tension timed contact angle measurements, respectively. The corresponding tab at the top selects a result page. The format of the results from surface tension measurements is different from those of contact angle measurements, meaning that the heading of the two result pages is different. If necessary, the page is switched automatically during measurements to show the measured values. The result table grows by inserting new results at the bottom. When full, the page will scroll upwards, and results that become invisible by this scrolling may be viewed by using the scroll bar at the right margin. The table will always scroll to the bottom when a new result is inserted.

The Results Window with the surface tension results tab



No.	Time	Gamma	Beta	R0	Area	Volume	Theta	Height	Width	Opt	Messages
Experiment: Test3 (Recalculation)											
1	0.000	42.13	0.447	1.387	36.63	22.26	91.32	4.131	3.058	1	
2	3.190	42.13	0.447	1.387	36.63	22.26	91.32	4.131	3.058	1	
3	6.320	42.13	0.447	1.387	36.61	22.25	91.40	4.128	3.058	1	
4	9.560	42.14	0.447	1.387	36.59	22.24	91.50	4.124	3.059	1	
5	12.69	42.15	0.447	1.387	36.57	22.23	91.59	4.120	3.059	1	
6	15.99	42.16	0.447	1.387	36.54	22.22	91.72	4.115	3.060	1	
7	19.23	42.17	0.447	1.387	36.52	22.21	91.83	4.111	3.061	1	
8	22.36	42.18	0.447	1.388	36.49	22.20	91.95	4.107	3.061	1	
9	25.71	42.18	0.447	1.388	36.46	22.19	92.02	4.103	3.061	1	
10	28.78	42.20	0.447	1.388	36.44	22.18	92.15	4.098	3.062	1	
	Mean:	42.16	0.447	1.387	36.55	22.22	91.68	4.117	3.060		
Std.dev.:		0.01	0.000	0.000	0.02	0.01	0.09	0.004	0.001		

The Results Window with the contact angle results tab



No.	Time	Theta (L)	Theta (R)	Theta (Avg)	Deviation	Messages
1		136.1	137.8	136.9	0.8	
2		125.5	125.8	125.7	0.2	
3		117.2	118.0	117.6	0.4	
4		110.8	109.2	110.0	0.8	
5		102.9	101.2	102.0	0.9	
6		92.2	94.3	93.3	1.0	
7		87.2	87.5	87.3	0.2	
8		80.4	81.5	80.9	0.5	
9		74.8	76.8	75.8	1.0	
10		69.1	70.9	70.0	0.9	
11		64.8	66.9	65.9	1.0	
12		59.1	59.7	59.4	0.3	
13		54.8	55.3	55.1	0.3	
14		51.7	50.6	51.2	0.5	
15		49.8	49.1	49.5	0.4	
16		46.4	47.1	46.7	0.3	
17		44.0	42.1	43.1	0.9	

Each result notebook table can contain an unlimited number of lines (only limited by the amount of memory/disk in the PC). Some limitations in the operating system may limit the number of lines that may be displayed. When the limit is reached, no more lines will be added, but the LOG-file will not be affected. Selecting the erase speed button (the rightmost button) will erase the whole table.

The Results windows are shown above. Independent of the results window, all results are also saved to separate **LOG files**. The name of this file is the same as the experiment (the parameter file), with the extension .LOG. (If there is a log file with the same name already in the result directory the file will be overwritten if Sequencing is off. If Sequencing is on, the log file name will be appended a number, starting from 1. Only unused file names will be applied). These files are ordinary text files and may be used to transfer results to other PC programs.

MAKING A MEASUREMENT

An ordinary measurement

To make a measurement you must have

1. An object to measure (!)
2. Measurement parameters
3. A measurement method

The easiest way to enter the necessary data for the measurement parameters and method is to use the New Experiment Wizard (see below). There are, however, several other ways to do this, and the user is referred to the sections about the Parameter and Method editors. There will always be an active set of parameter and method variables that are used if a new measurement is started in any of the "standard" ways, 1-3 below.

When the program is started, a **default** active set of parameter and method variables is used. The procedure of changing and editing these data will be described in the next paragraph.

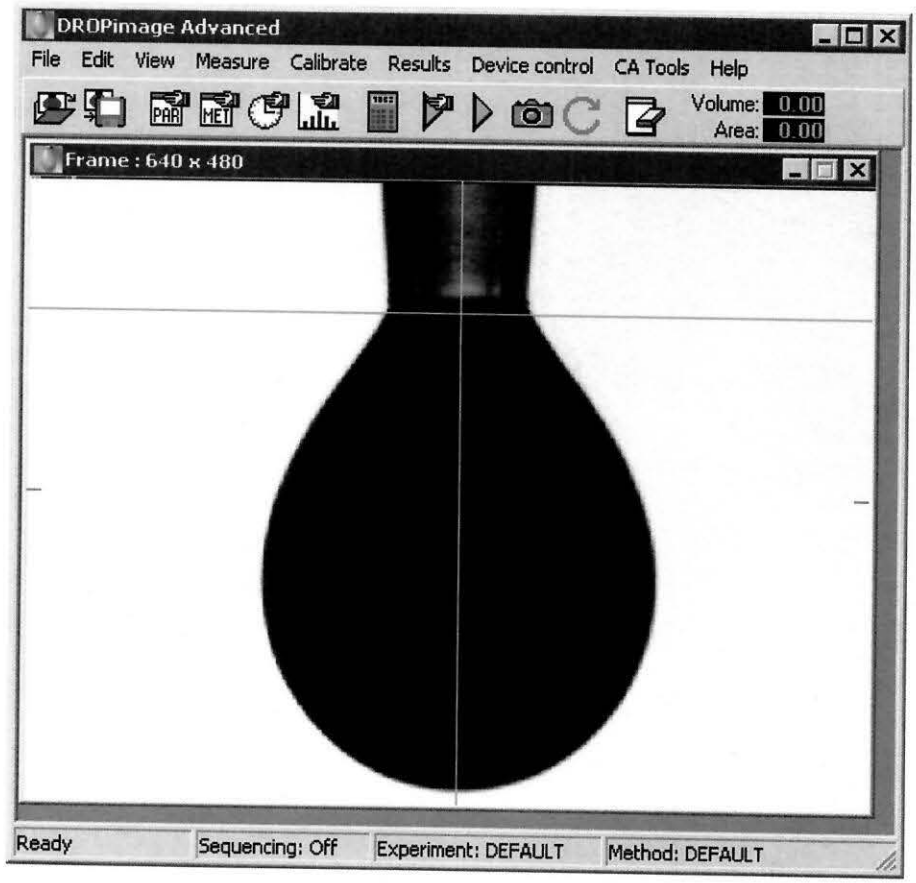
A measurement is **started** in one of several ways

1. Selecting Measure | Start measurement
2. Pressing Ctrl + m
3. Clicking the speed button  with the mouse
4. Clicking the Save & Measure button in the Parameter editor.
5. Clicking the Start button in the Select experiment dialog window.
6. Selecting Yes to start at the end of the New Experiment Wizard

In order to facilitate the easy visibility and selection of measuring parameters, a measurement may be started directly from Parameter editor, as in pt. 4 above. A measurement is then usually started by first opening the Parameter editor, by for instance clicking the speed button . You may then open a new parameter file, and/or set the correct parameters. The Save&Measure button then starts the measurement procedure. The Parameter editor will then be closed in order to avoid changes to the parameters during the measurement.

The measurement is NOT started immediately after this, but a picture is taken from the camera and displayed in the capture window. Also displayed are the selection **crosshairs** and the **Set cursor position** window, as shown below. The crosshair cursor is moved to the desired position (if not already there) and the Measure button is clicked, or the Enter key is pressed. The measurement sequence then starts. All measurements in the same experiment will use the same crosshair position.

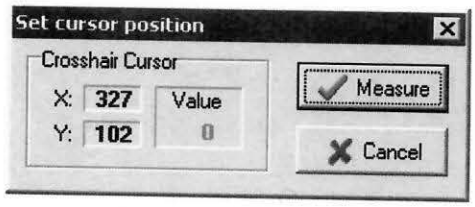
The Main window with the selection crosshair.



The crosshair cursor

The function of the crosshair cursor is to act as a reference for the edge detection ("filtering") routine. The vertical line always starts along the centerline of the image, while the start location of the horizontal line depends on the measurement parameters as specified in the Method (type of drop) and Parameter files (densities). For pendant drops the line will be either at the extreme top of the screen (normal pendant drops) or at the extreme bottom (upside-down drops). For sessile drops, the location of the horizontal line will also follow the density difference (positive or negative), but the line will start at the x-address specified in the configuration (.INI) file. At installation this value is 400, meaning 400 pixels from the top for normal sessile drops and 400 pixels from the bottom for upside-down drops (and bubbles). The crosshair may be moved by using the PC's arrow keys or by the mouse. One key-press moves the line 1 pixel in the corresponding direction. By holding down the <Ctrl> key, the cursor will move 10 pixels at a time. The crosshairs position will be saved to the next experiment.

The Set cursor position window



The edge detection routine uses the cursor coordinates in the following way (these rules do not apply to the calibration procedures):

a) Edge detection starts along the vertical hairline. This therefore should be approximately along the drop's centerline, but the exact location is not important for the program's data treatment, as the central axis is determined mathematically. An exception to this is when measuring contact angles by the extrapolation method, as the central axis is not important in this case. If both contact angles are selected, edge detection of both sides of the drop still starts along the vertical hairline, but if the right hairline is visible, detection of the left and right parts of the drop starts along the corresponding lines.

b) Edge detection starts either at the top or at the bottom of the picture; whatever edge has the **greatest distance** from the horizontal hairline. This means that if the line is **above** the middle of the picture, the routine starts at the **bottom**, and if the line is **below** the middle, the routine starts at the **top**. If the horizontal mask is visible (red line) the routine starts at the line. Note that the line has to be at the opposite side of the picture centerline as the horizontal hairline.

c) All edge detection is limited by the horizontal hairline, meaning that this line is used to mask the upper or lower part of the picture. According to rule b), this means that the part of the picture that constitutes the **smallest part** beyond the horizontal line is **neglected**.

d) The starting point of the drop profile is at the **first** point of **maximum contrast** (along the vertical line), meaning that other objects, or the drop inside, must either be masked by the horizontal line or have a lower contrast. Otherwise the program cannot detect the drop profile.

When measuring surface tension of a pendant or sessile drop, the Right Cursor group is not visible, it is only visible when measuring contact angles.

Use of the intensity trigger

The intensity trigger serves to synchronize the start of image acquire with change in the picture. This may for instance be the result of a drop falling to a surface, or appearing at the end of a capillary. This means that the intensity of most of the pixels at the drop's location will decrease, and the intensity trigger is therefore a high-pass threshold. The trigger is a short horizontal red line comprising of some (7) pixels at both sides of the vertical hairline, and at a set distance from the horizontal hairline in the direction of the picture's midline. This distance, as well as the intensity threshold, may be set in the Options dialog window (see "Options"). Use Trigger is selected in the Set cursor position window as shown above. When the experiment is started, the first picture will not be grabbed until the average intensity of the trigger line drops below the trigger value. If the intensity does not drop below this value, the program may wait infinitely. However, the experiment may always be aborted or started manually by means of the buttons in the Status window.

Filtering, calculation and results

The frame grabber board always digitizes the picture of the drop at the desired time. Then these data are "filtered", meaning that the drop profile is detected and stored in memory. The outline is plotted as white pixels in the drop picture, thereby confirming that the correct profile has been detected. If by some reason the profile is not detected properly, this will show up very clearly. In extreme cases, the profile may be completely missed, and an error message is produced; the reason for this is usually stray light in the picture, bad lighting conditions, movement of the drop or other objects in the picture too close to the drop surface. After profile plotting, the desired results will be calculated and presented in the Results notebook page. The results from surface tension measurements as shown in the Main window are explained in the table below:

The results from surface tension measurements

No.	Measurement number
Time	Time from start (seconds)
Gamma	The surface or interfacial tension (mN/m)
Beta	The shape factor
R0	The radius of curvature at the drop's apex (mm)
Area	The drop surface area (mm^2)
Volume	The drop volume (mm^3)
Theta	The contact angle at the drop limit (horizontal) hairline
Height	The total measured height from hairline to apex (mm)
Width	The maximum width = the diameter if Theta $\geq 90^o$ (mm)
Opt	The number of optimizations performed
Messages	Errors or other messages

Opt is explained in Appendix 1. The surface area and volume are calculated by numerical integration, assuming the drop is axisymmetric (as it should be). If the horizontal hairline is in the picture (i.e. not at the upper or lower edge), the area and volume is limited by this hairline. **Height** and **Width** are the pure experimental sizes. If the right and left sides are not equal (i.e. the drop is skewed) the height is the average of the two sides.

The contact angle shown here is calculated by interpolation of the theoretical profile represented by the values of Gamma (γ) and Beta (β) and the difference in the density parameters.

If a method controlled series of contact angles are measured (as selected in the "Type of drop" group), the contact angle is calculated by the curve fitting procedure given in the Options dialog (the default is the Circle method).

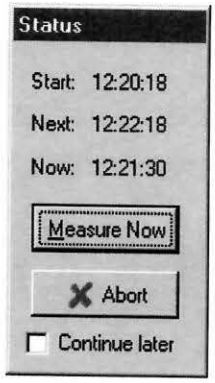
The results form a contact angle experiment are the left and/or right angle, the mean and deviation (mid-point) (if both left and right are measured), and the height and width of the drop.

If more than one measurement is specified by the method, these will be performed subsequently, and the mean value and standard deviation will be calculated (if the number is more than two).

Stop and continue measurement

When an experiment is running, the Measure Status window is displayed as shown below. Clicking the Abort button in the measurement status window may stop a measurement series. In the case more measurements were supposed to be taken, the experiment may be continued by selecting **Continue measurement**. In that case the new values will be added to the old values in the calculation of the mean and standard deviation. The same experiment may be stopped and continued several times.

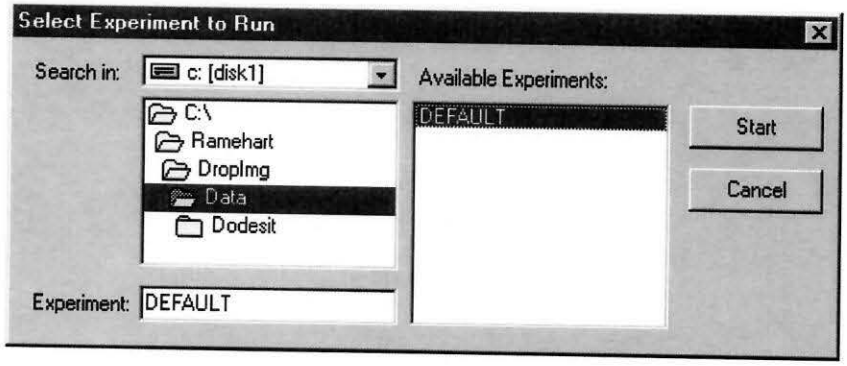
The Measurement Status window



Selecting an experiment

When a parameter file is saved from the parameter editor, or the experiment is started from the Save & Run button in the parameter editor, the saved parameters are automatically selected as active. As a shortcut, and in order to avoid the extra procedure if no changes are to be done to the parameters, the Select experiment function is included.

The Select Experiment dialog window



An experiment is selected either from the Measure menu or by the  speed button. In either case the Select Experiment dialog is opened.

The Start button loads and starts the selected experiment directly.

Sequencing

The sequencing function is connected to the storage of experimental results. All results from experiments are automatically saved to a log-file. This is a text-file with the experiment's name and type .LOG. If a new experiment is run with the same name as an old one, the new log-file overwrites the old, if Sequencing is **off**. If sequencing is turned **on**, however, a new file name is created by adding an underline character (_) and a number to the experiment's (parameter) name. The number is started at 1 and new numbers are selected consecutively so that no existing file is overwritten. "Gaps" created by deleting files are filled before new numbers are added at the end. The Sequencing field on the main window's Status bar shows if Sequencing is turned on or off. Sequencing is turned on and off from the Measure menu (Sequencing on or Sequencing off) or by pressing Ctrl+Q. This is a toggle that turns Sequencing on or off, depending on its present status.

Oscillation Measurements

DROPimage Advanced is able to calculate surface dilatational elasticity and viscosity of surface films by means of oscillatory measurements. For this purpose, a volume control device is needed, either the Ramé-Hart auto syringe or a dedicated oscillation unit. The latter is necessary in order to use frequencies above ca 0.5 Hz, but satisfactory results are often obtained by just using the auto syringe. Below will described how such measurements are done, and at the end of the chapter, a brief account for the theoretical background for this type of measurements will be given.

The oscillatory measurements are based on sinusoidal, or near sinusoidal, drop volume variations with time.

Activating Oscillation capabilities

The Oscillation capabilities of DROPimage are hidden by default, because the average user does often not use these types of measurements. A setting in the initialization file (DROP.INI) activates the capabilities.

```
[Oscillator]
OscillationMenu=1
```

Different aspects of the oscillation procedures are controlled by several other lines in different sections the ini-file control. These will be described in the corresponding sections.

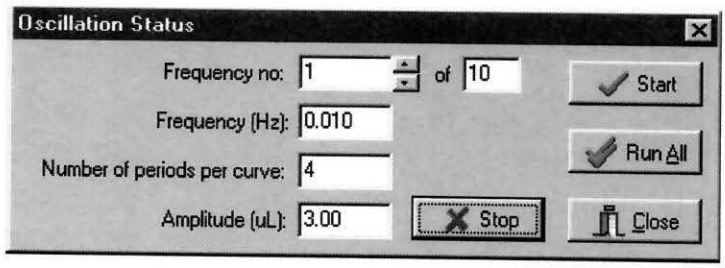
When Oscillation is activated, new features will become visible in DROPimage:
1. A new line in the Measure menu of the Main window.
2. A new button in the Type of measurement group in the Method Editor.

3. The Oscillation control check box in Installed options in the Options window will be enabled.

Oscillation experiments are controlled by the different parameters of the Method that are accessed from the Method editor. They are described below under the **Method editor** section.

Running an Oscillation experiment

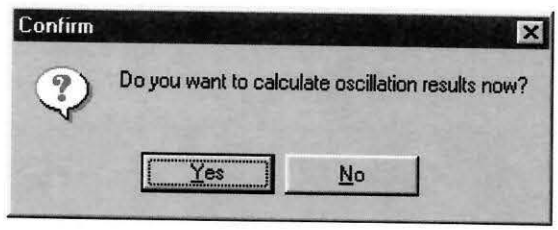
Oscillation Status dialog for control of oscillation runs



An Oscillation measurement sequence is started in the same way as other measurements. The crosshair cursor is adjusted and the Start button is pressed. The run is not started immediately, but rather the Oscillation Status dialog appears as shown above.

From this dialog box, you may run one single frequency at a time or all frequencies consecutively. If you just press the Start button, the program will run one frequency at a time, according to the values in the frequency list in the Method. The Frequency no will increase automatically, but you may change this sequence any time by using the up/down control arrows. You may thus, if you wish, run the same frequency several times for better reproducibility. If you hit the Run All button, all frequencies will be run automatically in sequence. The Time interval in the Method will be used as the time interval between oscillations (frequencies).

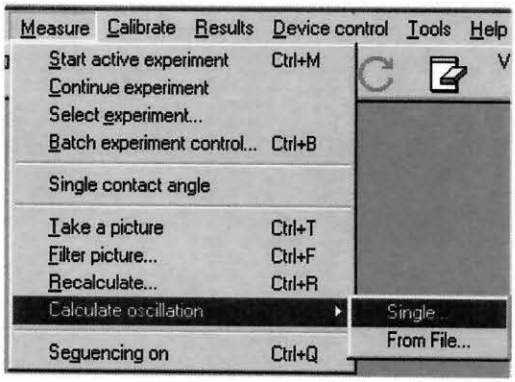
When the last frequency is finished, the program will ask if you want to stop and will then prompt:



If you answer Yes to this, all results from the present series of frequencies will be calculated and displayed. This will be further described in the next paragraph.

Calculating Oscillation results

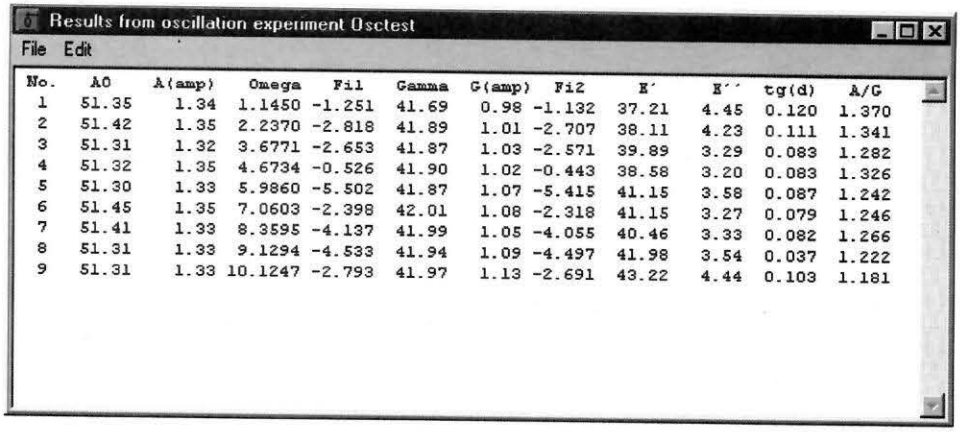
Oscillation results may be calculated immediately after the experiment is finished as described above, or may be calculated any time after that, as long as the LOG-files are preserved. Calculation is selected from a separate line on the Measure menu, which appears when Oscillation is enabled, as shown below.



Calculate oscillation has a submenu with 2 choices, either Single or From File. The Single choice opens a dialog box where you can choose a single LOG-file that contains the surface tension results at one frequency. Any LOG-file may be selected, but results will only be meaningful if the LOG-file contains oscillation data. There is no external difference between LOG-files, except for the name, so the user should take a note of the file name that appears in the Results window before each table of results (except for the LOG-extension). The program marks the LOG-files belonging to one experiment by adding the frequency number to the file name, but before any sequence numbers. For example, the LOG-files from experiment Osctest will have LOG-files named Osctest1.LOG, Osctest2.LOG etc. without sequence numbers. Sequencing will add an underscore followed by the sequence number, for instance Osctest1_1.LOG, Osctest2_1.LOG etc.

The From File choice leads to the same type of calculation that may be done immediately following the experiment. This function uses a special text file that lists the names of the LOG-files belonging to the experiment. The text file has the type OSC and choosing this function lead to an Open File dialog where you may choose an OSC-file. The program will then calculate all LOG-files listed in the OSC-file. The results will be presented in a separate window as shown below.

Oscillation results window



No.	A0	A(amp)	Omega	Fi1	Gamma	G(amp)	Fi2	E'	E''	tg(d)	A/G
1	51.35	1.34	1.1450	-1.251	41.69	0.98	-1.132	37.21	4.45	0.120	1.370
2	51.42	1.35	2.2370	-2.818	41.89	1.01	-2.707	38.11	4.23	0.111	1.341
3	51.31	1.32	3.6771	-2.653	41.87	1.03	-2.571	39.89	3.29	0.083	1.282
4	51.32	1.35	4.6734	-0.526	41.90	1.02	-0.443	38.58	3.20	0.083	1.326
5	51.30	1.33	5.9860	-5.502	41.87	1.07	-5.415	41.15	3.58	0.087	1.242
6	51.45	1.35	7.0603	-2.398	42.01	1.08	-2.318	41.15	3.27	0.079	1.246
7	51.41	1.33	8.3595	-4.137	41.99	1.05	-4.055	40.46	3.33	0.082	1.266
8	51.31	1.33	9.1294	-4.533	41.94	1.09	-4.497	41.98	3.54	0.037	1.222
9	51.31	1.33	10.1247	-2.793	41.97	1.13	-2.691	43.22	4.44	0.103	1.181

In the results window, the following results are given:

A0	The mean surface area (mm^2)
A(amp)	The area amplitude, ΔA (mm^2)
Omega	The angular velocity, ω (radians/s)
Fi1	The shift in start of the area curve from measurement start (radians)
Gamma	The mean surface tension, γ (mN/m)
G(amp)	The surface tension amplitude $\Delta\gamma$ (mN/m)
Fi2	The shift in start of the gamma curve from measurement start (radians)
E'	The storage elasticity module
E''	The loss elasticity module
tg(d)	Tangent to the phase angle between A and Gamma, tan(δ)
A/G	The ratio A(amp)/Gamma(amp)

The results may be copied to the clipboard, saved to a file, etc. The results are not saved by default, but may be recalculated any time as long as the OSC-file and the LOG-files exits. If plotting is enabled, the modules (E' and E'') will be plotted as a function of frequency.

Oscillation hardware

The program is set to use one of two different hardware units to control the oscillations. These are the Ramé-Hart Auto syringe or the specially constructed oscillator. Which unit to use is set in the Method (se the Method editor section). The oscillator is faster than the auto syringe (up to ca 10 Hz).

When using the auto syringe, a measurement is taken at each volume step, which means that the volume at each point will be changed in one step from the last point. In order to obtain a near sinusoidal curve, the number of points per period should not be much below 10. However, experiments have shown that the

complex module may be measured fairly well even with a lower number of points, while the phase angle will be less accurate, the less number of points (see the end of this chapter for definitions). This will have most significance only if the phase angle becomes appreciable (-> 45 degrees). For mainly elastic films, elasticity will be well determined with a low number of points per period.

When using an oscillator, the motor will run continuously during each frequency period, so step lengths will be less of an issue here. If the oscillator has manual stroke control, the Amplitude field will have no influence on the actual volume amplitude.

If an oscillator is installed, this may be selected in the Options menu. The corresponding line in the ini-file is in the `[Installed]` section where setting

```
OscillationControl=1
```

will enable the oscillator. (In the time of writing, an automatic oscillator is presently only available as a prototype, on special request). It is also possible to use a manually controlled oscillator (not controlled by DROPimage) by setting

```
ManualOscillator=1
```

in the `[Oscillator]` group. You will then have to set all the parameters of the oscillator manually; these should correspond to the values set in the Method. The oscillator is run manually when the Oscillation Status window is open (see below), and each measurement is taken when the Start button is pressed in this window. This feature is made available for especially interested researchers only, who want to construct their own hardware.

There are additional lines in the `[Oscillator]` section for the automatic oscillator, but these will not be described here. Please refer to the Oscillator Manual.

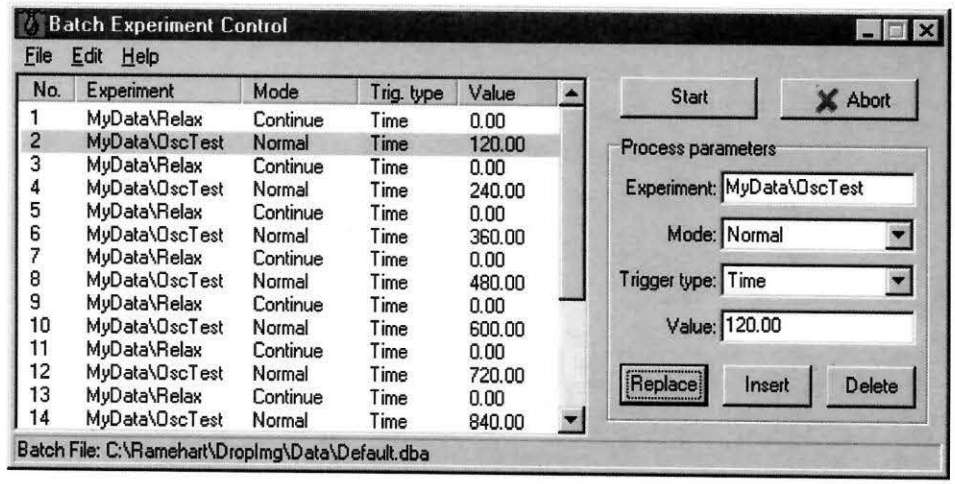
Batch experiments

Batch experiments are a facility that makes it possible to run a sequence of different experiments automatically. DROPimage will go thru the list of experiments in the Batch Experiment Control window.

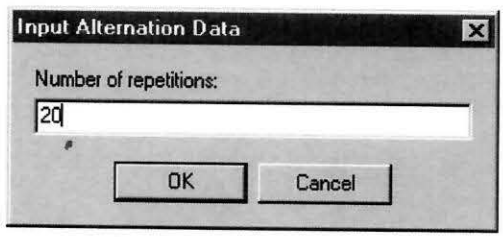
The list contains records containing experiment Names, Mode, Trigger type and Value. The Name may contain directory name(s) separated from the Parameter name by a backslash in the ordinary way as shown in the figure. Mode is either Normal or Continue. Continue means that the experiment will be continued from where it was interrupted, when repeated next time in the list. There may be one or more Normal experiments in-between. Only one experiment may be continued at

a time. Trigger type is either Time or Surface tension, and Value is the value of the trigger. When the trigger is Time, the value is in seconds, and in case of Surface tension, the value is in mN/m. When the value of the trigger is attained, DROPimage turns over control to the next experiment in the list. In the case of surface tension, the measured gamma must drop below the trigger value.

The Batch Experiment Control window



The records in the Batch Experiment Control are added, deleted and edited in the Process parameters group box. In order to make it easier to make alternating experiments, there is an Alternation function available from the Edit menu.



The program asks for the number of repetitions and the trigger interval between them. It then copies the number of repetitions of the first 2 lines, with the desired trigger interval. You may then edit the values as desirable.

The records in the Batch list may be read from a file and saved to a file by the functions on the File menu. The file type will be .dba and they are ordinary text files. When the Batch Experiment Control is first opened, it will read the records form the Default.dba file.

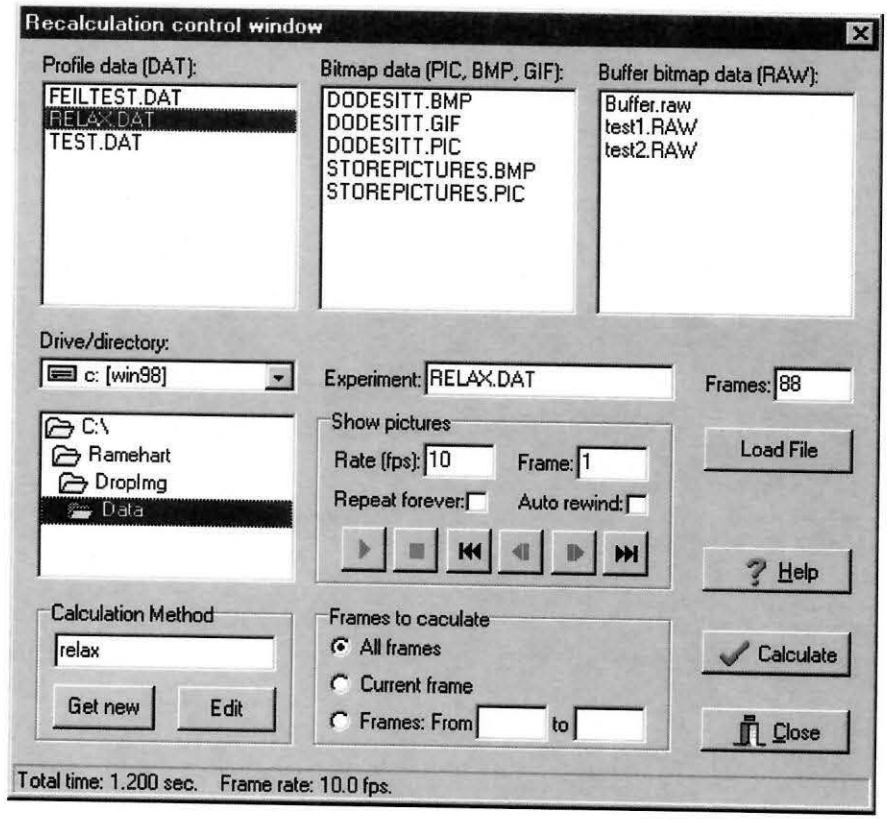
The batch facility has been written especially to make it possible to run intermittent oscillations or step functions. In the case of intermittent oscillations as in the figure shown here, the results will be appended to a LOG-file named from the experiment (here OscTest), and ending in "_osc.LOG".

Recalculation

If picture data have been stored in advance, either as full bitmaps or as "filtered" profile coordinates, (re-) calculation will be possible. The method used for re-calculation should be a so-called **Recalculation method**, meaning that the Data source field in the method is set to Disk file instead of the ordinary Video option. This means that the program will take data from a file instead of the video camera.

You may use the **same** method as used in the measurement or make a **new** method for recalculation. The latter is recommended if you want to change some of the fields in the method, such as Calculation, Report, Number of measurements, etc. If you use the original measurement method for recalculation, the program will automatically set Data source to Disk file.

The Recalculation control window.



If you use a separate method for recalculation, the Data storage field in the two methods must be corresponding in a way that makes recalculation possible. This usually means that they must be equal, or at least two of the checkmarks must be in the same boxes. The program will prefer to use Profile data, if available. Any

kind of experiment that has stored picture data may be recalculated; prior calculations or missing calculations are not taken into consideration.

Recalculate is selected from the Measurement menu, or by pressing  (the calculator button). The Recalculation control window will appear to let the user select the file (parameter file). The window is shown below.

This Recalculation control window serves as control center for the display and selection of experiments to recalculate. You can find all experiments that contain image data either in the form of profiles (DAT), separate pictures (PIC, BMP, GIF) or image buffer files (RAW). You load a file by selecting the file in the list and clicking the Load File button. You may also double-click the file name to load the file immediately.

When the file is loaded, the transport buttons in the Show pictures group and the Calculate button are enabled The first picture will be shown either in the Main application window or in a special Plot window in the case of profile (DAT) files. The number of frames is also shown in the Frames edit box.

In case the program cannot find the corresponding Parameter file, the Calculate button will be disabled, and you cannot recalculate the experiment. You may, however, still view the image data. The program will look for the Parameter file in the current directory and in directories above the current one. *You should therefore store data files for recalculation either in the same directory as the Parameter file(s) or in subdirectories.*

The *transport buttons* are used to view the pictures either as a **video** or as **single frames**. You may get button *hints* by just holding the mouse cursor over a button. The green arrow (▶) starts the video sequence and the speed of the video is given by the Frame rate box (fps = frames per second). The blue arrows (◀▮ ▮▶) **step** a single frame either forwards or backwards. The red stop-button (■) **stops** the video immediately at the current frame. The black Home and End arrows (⏮ ⏭) bring the frame position to the **first** and **last** frame, respectively. *The maximum fame rate that is achievable is dependent on the PC's specifications and the file format. For bitmap images, the RAW format usually gives the highest frame rate.*

The two check-boxes above the transport buttons select if the video should repeat continuously or if the video should be rewound after the last frame. The boxes may be checked or unchecked while the video is running.

The Frames to calculate group selects the frames to recalculate, all frames, the current frame, or a group of frames given between and including the From and to frames. In the Calculation Method group, the Method that belongs to this experiment is show. You may use the Get new and Edit buttons to select another Method for the calculation and you may start the Method editor from this window by clicking the Edit button.

When you have selected the frames you want to recalculate, click the *Calculate* button. When bitmap data is used for recalculation, the program displays the crosshair cursor. The function of the crosshair cursor is the same as with an ordinary measurement. All subsequent data points within the same experiments will use the same cursor position. To make special adjustments, you must calculate the frames separately. The results from the calculation are shown in the ordinary Results window, and a log file is produced in the usual way.

If the conditions as described above are fulfilled, recalculation can conveniently be used to evaluate for instance the effect of changed parameters (i.e. calibration, densities) or to get faster measurements. Also, an experiment that makes measurement over long time intervals (several hours) will be much more safely conducted by only saving pixel data in real-time and doing the calculations later. Often conditions may change considerably during a long run, electric noise may disturb the filter routine, pendant drops may fall off, sessile drops may become too flat, etc. It should, however, be kept in mind that stored data (especially pixel data) takes up a lot of disk space. If the **same experiment name** (parameter file) is used again without changing the data path or otherwise backing up the data, the old files will be **overwritten**. This may be an advantage if used on purpose (saves space), but care must be taken in order to avoid unwanted data loss.

Oscillation experiments can only be recalculated **one frequency at a time**. Select the picture file that corresponds to the desired frequency. The frequencies are numbered by sequence from 1 and up, and the number is in front of the underline (_) that separates the ordinary sequence numbers from the experiment (parameter) name. Example: Osc3.PIC denotes the pictures from frequency #3 in the Osc experiment. (The picture numbers in brackets are removed from the file list).

The **actual time** for a measurement may not always be exactly the time that was scheduled; a time file and method may be also changed after the experiment is finished. Because of this, the program saves the actual times for each measurement that stores data (in pixel or profile-data form) in a special file, a so called **Real Time file** (type = `.RTI`). When doing recalculation, the time values are taken from this file, and not from the method's calculated time values or the regular time file.

MEASURING CONTACT ANGLES

Three different locations

The DROPimage Advanced program can measure contact angles at tree different locations in the program:

1. Contact angles are always measured as a part of the surface tension measurements. This procedure utilizes the full **theoretical drop profile** as described by the Laplace equation. The result may be considered quite reliable if the fit of the theoretical profile is good. The disadvantage of this procedure is that the drop should be symmetric, and the angle will be the same at both sides of the drop. Also, the whole drop must be visible and the contact angle cannot be lower than ca 45 deg.

2. The second location is Method controlled measurements when the Type of drop is Contact angle. In this case a pure **geometric** extrapolation that uses no theoretical description of the drop profile is used, and this is therefore less accurate. However, it has other advantages; it can measure either one or both sides of the drop independently, and the whole drop does not need to be visible. Disturbances in the image (for instance a pipette) can be masked. There are 3 different methods available for this procedure; the Circle, Secant, and Linear method. The first uses a curve fit to a circular profile, the second an extrapolated secant, and the third a pure linear fit. The Circle method is usually the most accurate, and is the default. The Linear method should only be used to measure straight edges (not drops). The procedure is not dependent on absolute calibration, i.e. it is independent of the image's magnification, but the aspect ratio must be correct in order to calculate the correct angle. If the droplet phase is "Air" or "Gas", the contact angle will be converted to its complementary angle (180^{o} - θ). This procedure will also produce a Log-file in the usual fashion that will use the name of the active Parameter file.

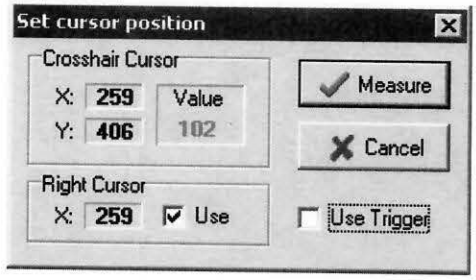
3. The third location is the **Contact Angle tool** (CA tool) that is available on the CA Tools menu. This tool uses the geometric procedure as outlined above, but is a pure manual tool, equal to the corresponding tool in the DROPimage Standard program. The CA tool produces live contact angle records directly thet may be saved as Contact Angle files. These files may also be read into the CA tool. The CA tool is described in detail below.

Method controlled measurements

The function of the cursor lines

When the experiment is started, the video picture is presented on the screen. The crosshair cursor is used in a special way here; the horizontal solid/gas interface must be aligned with the horizontal cursor line, as this line determines the mathematical surface where the contact angle is measured. In order to move the horizontal line, you must hold down the <Shift> key, thus the left and right cursors may be moved independently by holding down the left and right mouse buttons, respectively, without affecting the horizontal line. Alignment may be most conveniently achieved by first focusing on the front edge of the solid (this

should be a sharp edge) and aligning this with the cursor line, then focus is shifted to the drop profile. If you use the Contact Angle tool, the baseline is usually set in the Setup dialog, using the *Snap* button in this window. When measuring contact angles by a Method controlled experiment, the Set Cursor dialog looks somewhat different, as shown below.



The Right Cursor checkbox switches on or off an additional vertical line that is controlled by the right mouse button. The vertical cursor lines limit the measurement region, so that the regions to the right of the left cursor and to the left of the right cursor are excluded. This means that when both cursors are used, the region between the cursors is excluded. This may be used to mask the capillary (syringe needle) that is often used in contact angle measurements.

The Left and Right checkboxes in the Measure group, selects which side of the drop should be measured. You may select one or both sides.

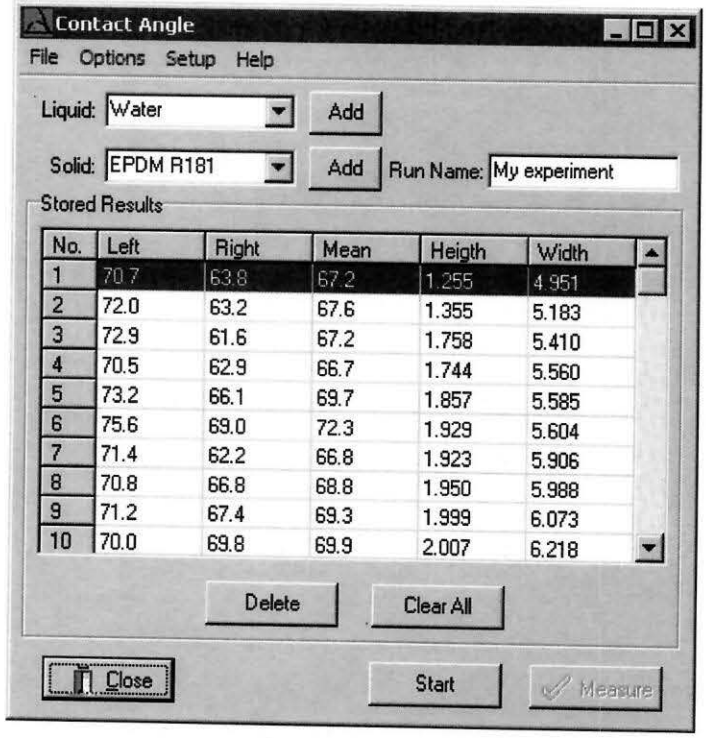
Measurement

Clicking the Measure button does the measurement itself. The drop profile is detected, and the angle with the horizontal cursor line at the point of contact is calculated by numerical extrapolation. The values are shown in the Results window, in the contact angle page, and in order to visualize that the correct angle is measured, the tangents at the point of contact are plotted in the main picture. If both sides are selected, the **average** contact angle and the **deviation** are also calculated (deviation = ½ of the difference between the two).

Using the Contact Angle tool

Selecting the Contact Angle tool opens the Contact Angle window. The window is shown below.

The Contact Angle tool window.



The Contact Angle tool window has its own menu at the top.

The Contact Angle menus

File

Open
Opens a Contact Angle (CA) file and **adds** the data to the bottom of the Stored Results table.

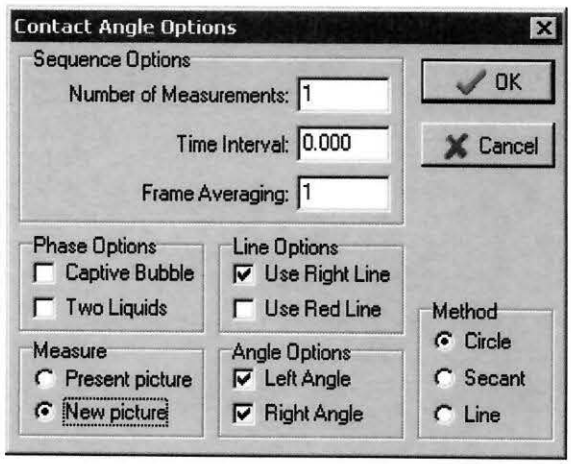
Save As
Saves **all** the data in the Stored Results table to a Contact Angle (CA) file.

Generate Log
Saves all the data to text file. The file extension is TXT.

Options

Opens the Contact Angle Options dialog.

The Contact Angle options dialog window is used to set the basic control parameters for the measurement(s). The Contact Angle options are remembered between runs.



If the **Number of Measurements** is more than 1, the Time Interval is used between each measurement. If Time Interval is below 0.04 s, the frames are acquired as fast as possible.

Frame Averaging sets the number of frames used as an average in each measurement. The frames are acquired as fast as possible, usually 30 (U.S., Japan), or 25 (Europe, etc.) frames/sec. This averaging should not be confused with the Number of Measurements. The total number of frames acquired is the Number of Measurements x Frame Averaging.

Captive Bubble selects measurement of captive bubbles. The contact angle will be calculated as the outside angle (in the liquid).

Two Liquids selects the measurement of a oil in water or water in oil system. When this box is checked, a new drop-down box appears in the Contact Angle tool. The box, named Ext.phase, is used to select the external phase. Two liquids are used in the Solid Liquid Liquid Surface Energy tool.

Use Right Cursor turns on and off the Right vertical line.

Use Red Line turns on and off the horizontal Red-line. This line limits the Region Of Interest (ROI) for the measurement.

In the **Measure** group box the actual picture and angle(s) are set. If **Present picture** is selected, the picture already in the Main window is used. This makes it possible to measure saved pictures.

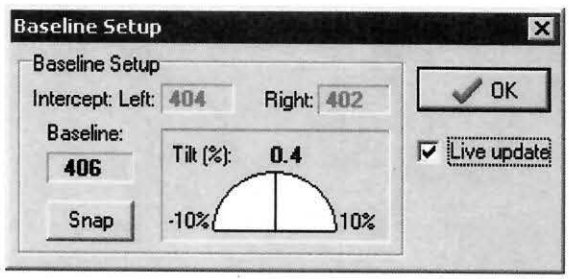
In **Angle Options** you select which angle(s) that is to be measured.

The **Method** group selects which extrapolation method to use for the contact angle calculation:

- The **Circle** method, which is the default, will normally be the best.
- The **Secant** method (used by the original DROPimage program) uses an extrapolated secant, and may be better for very large drops, where the edge deviates much from circularity.
- The **Line** method uses a straight line fit, and is only to be used to measure straight edges (not drops), for instance for calibrating purposes.

Setup

Opens the Baseline Setup dialog as displayed below.



The Live update check box selects if the image is updated continuously (ca 2 fps) with the values in the Setup dialog (in that case, the main image will be blinking). You may instead update the image manually by clicking the camera icon in the Main window. The values are updated independently of the Live update selection.

When the Setup dialog shows, all 3 cursor lines (horizontal, left and right) will appear in the Main Window. The two vertical cursor lines will appear close to the edges of the image. The two **Intercept** boxes in the Setup dialog show the intercept between these two lines and the horizontal line. The **Baseline** box shows the location of the baseline. All values are given in pixels from the top.

The **Tilt** indicator measures the tilt of a line through the two intercepts (the tilted line is NOT shown). You can adjust the left and right cursor by the mouse, holding down the left or right button, respectively. The objective is to adjust the image to obtain the minimum (i.e. close to zero) tilt. The tilt will usually be

adjusted by either adjusting the Goniometer's stage, the sample, or the camera's tilt (if the stage is already horizontal).

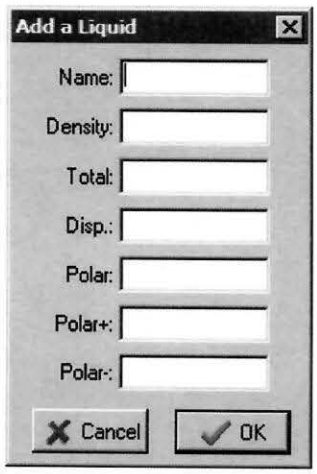
The Snap button moves the horizontal line to the mid-point between the two intercepts.

The tilt measured may be dependent on the image's contrast. The contrast is adjusted in the View | Video setup dialog.

All intercepts are calculated by the maximum gradient method.

Pulldown boxes

The pulldown combo boxes contain the name of the liquid and solid. The names are taken from the files LIQUIDS.TXT and SOLIDS.TXT, respectively. A new liquid or solid may also be added by clicking the corresponding Add button. This brings up the Add dialog:



You must add at least the name of the liquid (or solid) and the Total surface tension. The other surface tension components are only necessary for liquids, and which ones are dependent of which of the surface energy tools are being used with the liquid.

These parameters may also be added and/or edited by the Phase Editor (Edit | Phase Editor).

Run name

The run name is voluntary and is only used to identify the experiment. In the case the Solid Liquid Liquid (SLL) Tool is going to be used with the contact angle

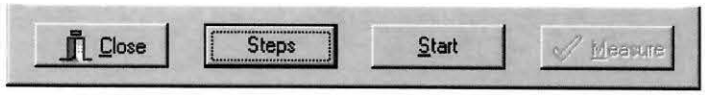
data, the Run name box should contain the surface tension of the liquid (however, it is possible to enter the surface tension later, in the SLL Tool).

Stored Results table

The table is filled with the results, sequentially. The Delete button is used to delete the item under the cursor, and the Clear All button clears the whole table. Contact angle files that are loaded into the program, are appended to the bottom of the table. The data in the table are saved between runs in a special file.

Stepping

If the Rame-Hart auto syringe is present in the system, the lower part of the Contact Angle tool window will contain an extra button denoted Steps:



When the button is pressed, the lower part of the window is expanded. The two Stepping buttons are initially greyed, but are activated when the Start button is pressed. The lower part of the window then looks as shown below:

The two buttons are self-explanatory, and are intended for the measurement of advancing and receding contact angles, as denoted in the group box's caption. The **Delay time** is the time (in milliseconds) between the (start of the) actual step and the measurement. The measurement used the values of the **Number of measurements** and **Frame averaging** in Contact Angle options at each step.

NEW EXPERIMENT WIZARD

The easiest way to set-up a new experiment is to use the New Experiment Wizard. A new experiment may also be started directly from the Wizard. In this section the use of the Wizard will be described, while a more detailed description of Parameters and Methods and all Parameter- and Method fields will be given in the next section.

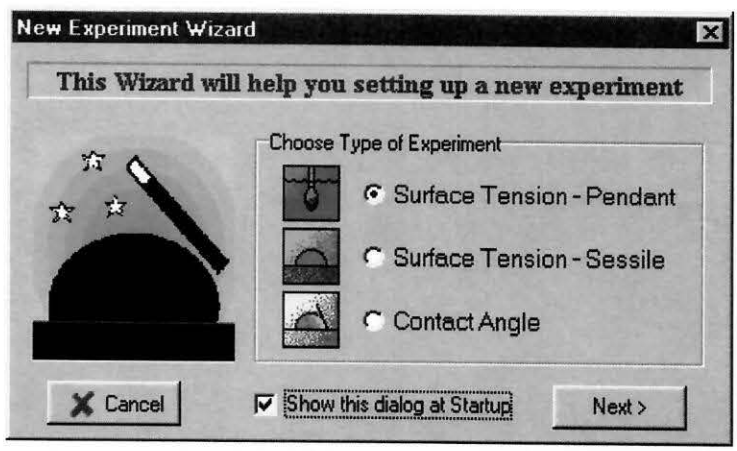
Some important properties of the Wizard should be noted:

1. The Wizard will make one new Parameter file and one new Method file. These files will have the same name (and the types PAR and MET, accordingly).
2. The Wizard will set only the most important fields in the Method. For the other fields, default values will be used, i.e. the values in the Default.MET file will be used. This also includes the data file directory name.
3. After having used the Wizard, the fields of the new Parameter and Method files may be changed in the ordinary way, by using the Parameter and Method editors, accordingly, as described in the next section.

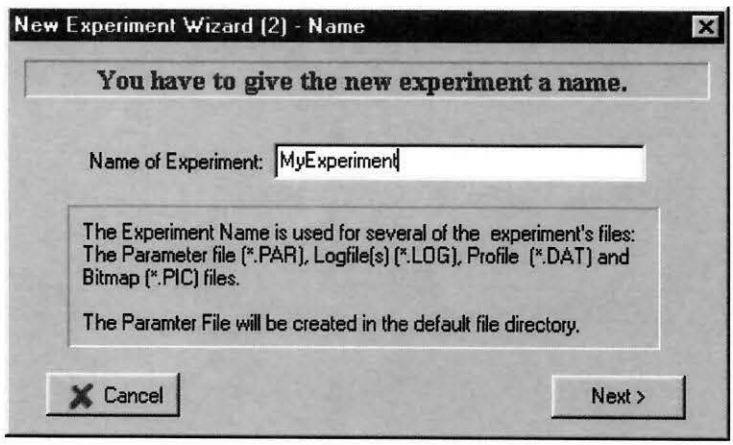
How to use the Wizard

The Wizard may be set to start automatically when DROPimage Advanced is started, by checking the corresponding check box as shown in the figure below. At any time the wizard is also available from the File Menu (the first line). The introductory screen looks as shown below.

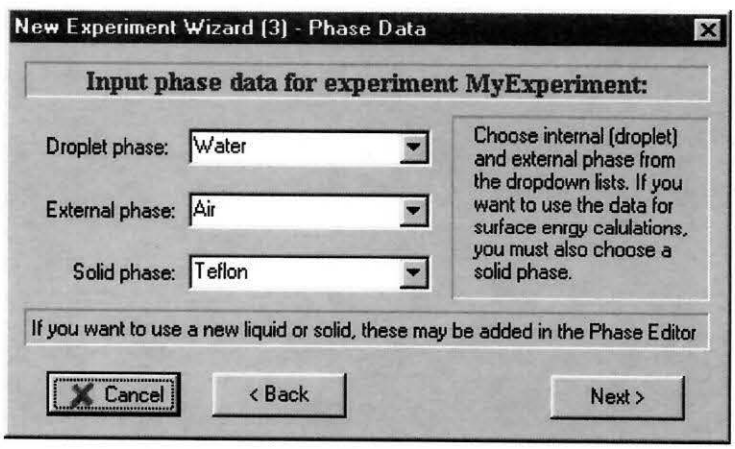
In this screen you select the type of experiment. Pressing the Next button takes you to the Name screen.



The Name screen should be self-explanatory. As mentioned above, both the Parameter and Method files, together with all the data files, will use this name. If you select a name that already exists, the Wizard will ask if you want to overwrite this experiment, which means you will not be able to use that file as a matrix for your new experiment. If you don't want to overwrite the file(s) you must either use another name, or press the Cancel button.

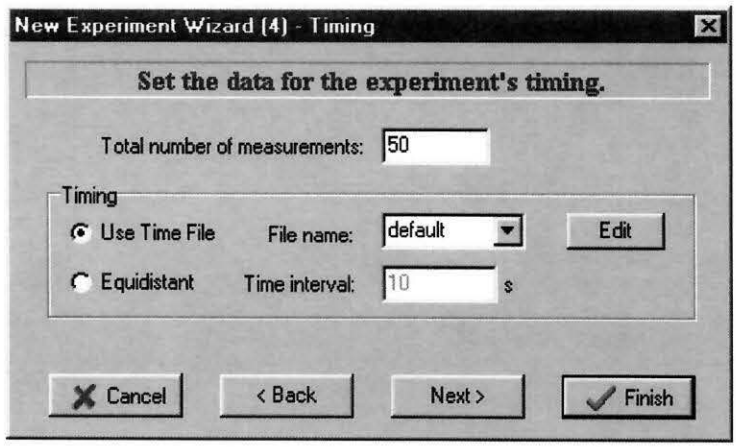


The Next button leads to the Phase Data screen where you select the name of the phases. The corresponding densities will be taken form the Liquids.TXT file.

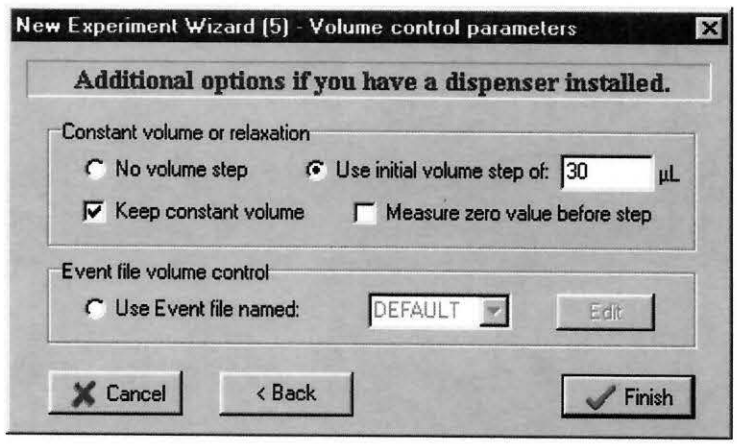


You may go back to the Name screen from the Phase Data screen; the Next button takes you to the Timing screen, where you set the number of measurements and the values for the experiment's timing. If you want to use a Time File, pressing the Edit button will start the Time File Editor. If you save the data in that editor under a new file name, the new name will appear in the Wizard's File name box.

If you have no auto syringe installed in your system, the Timing screen will be the last one displayed, and you may complete the wizard by pressing the Finish button (there will be no Next button).



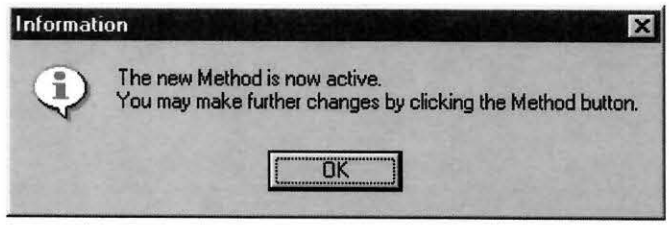
If an auto syringe is installed, the Next button will be visible, which will take you to the Volume control parameters screen. This screen treats the volume control parameters somewhat differently than the Method editor and is intended to make the setting of those parameters more intuitive.



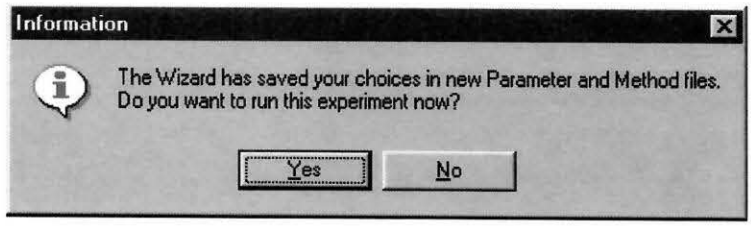
The two group boxes are mutually exclusive, meaning you are able to select fields in only one of the groups. In the upper group selecting the No volume step button produces an ordinary timed experiment. You may, however, also select the Keep constant volume check box here. Selecting Use initial volume step sets up a relaxation experiment.

The lower group selects an Event file to be used with the experiment. The Event file will be the same as the Time file, and you may also start the Event editor from this Wizard screen. Saving the Event file under a new name will also change the name in the Event file name list box.

When you are satisfied with your choices, press the Finish button. The following information message is displayed:



When pressing the OK button, you will be presented with the option to run the new experiment right away.



If you select Yes, the experiment will be started in the ordinary way. If you select No, you will return to the Main screen, but as displayed, the new Parameter and Method files will be active. You may choose to edit the new Method further, start the experiment later, etc. If you want to put the data files in another directory than the default one, you should edit the Data directory box in the Method editor.

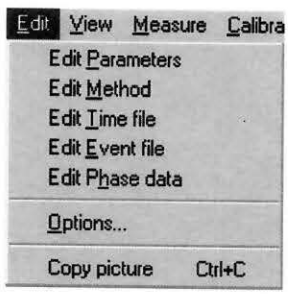
ENTERING AND EDITING CONTROL PARAMETERS

Measurements are performed using the active set of constants that control all aspects of the experimental procedure and calculations. These include the parameters entered through the Parameter editor and those controlled by the Method. In addition, the measuring time and special events (like volume steps) are edited in a separate (or rather two separate) editor(s). Most aspects of the measurement are controlled by the **Method**. This includes type of measurement, calculation, presentation etc. The Method **name** is one of the measurement parameters. The parameter file is the file that refers directly to the experiment, and the experiment's **name** is equal to the **Parameter file name**. This also means that this name is used for the log file(s), bitmap files, profile data files etc. that are directly connected to the experiment. File naming conventions are described in a later section. The different fields in the Parameter, Method and other menus are described below, after the Edit menu description.

Edit menu

The Edit menu is shown below. It consists of 3 groups with 5 items in the first group and 1 each in the other two. The 5 first selections each lead to a separate editor. In these editors the key parameters that control all the measurement sequences, calculation and presentation may be defined and changed.

The Edit menu

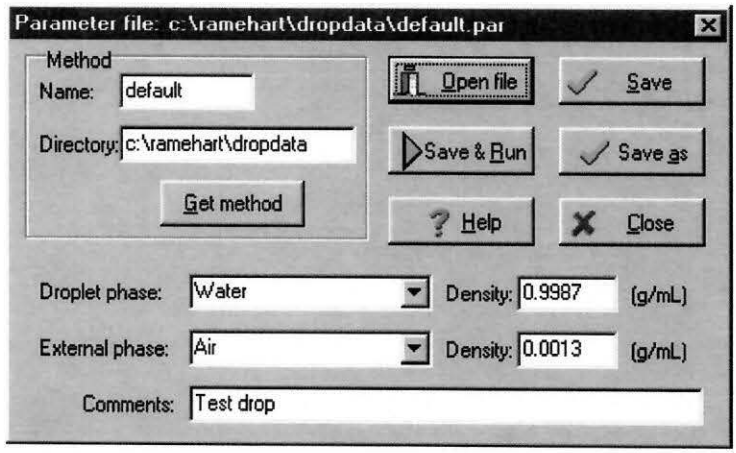


In addition to the Editor lines, the Edit menu contains the **Options** and the **Copy picture** selection. These items will be described after the editors' section. The Parameters, Method and Time file editors can also be reached directly by a speed button. The file selection dialog will then be skipped, and then editor will be opened with the active file. When Edit <name> is selected, a standard Windows dialog box is first shown that prompts for a file name. When a file is selected, the editor window is shown. The editors are described below.

Parameter editor

The Parameter editor window is shown below. The name of the parameter file is shown in the window's title bar.

The Parameter Editor



Method

The first field is the Method file that may either be typed in or selected by clicking the Get method button. This opens a file dialog box to navigate and select the method.

External phase, Droplet phase, Solid phase

The most important fields are the Droplet phase and External phase with the two Density fields. The program contains a list of phase names (liquids and gases) with corresponding densities (the **liquids.txt** file). The Solid phase is used in contact angle files for application in the surface energy tools. The Solids are taken from the **solids.txt** file. The solid is not used in surface tension measurements, but is important for making contact angle files to be used in the surface energy tools. All three phase boxes are combo boxes that contain a dropdown list from which the correct phase may be selected. The corresponding Density field will be automatically filled in. To enter and edit the list of phases, use the **Phase editor** that is described below.

Density

The most important fields are the two Density fields. The densities are required data that the program uses to determine the measurement geometry (ordinary or upside-down drop or bubble) and to make the calculations. The densities may be written directly into the edit boxes, or automatically from the phase dropdown lists (see above).

Comments

The Comments field is only for entering comments that are to be included in the report (see below). The comments will not appear elsewhere. This field may be left blank.

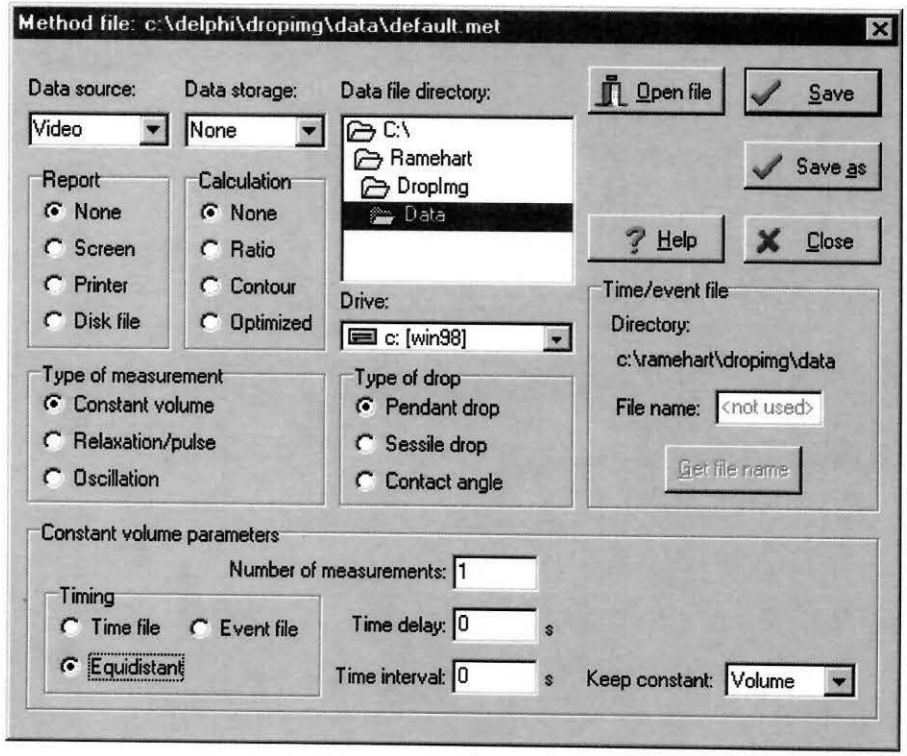
It is important to note that the edge detection routine and calculation procedures will perform according to the sign of the density difference and the type of drop (pendant or sessile). For pendant drops, if the density of the drop is larger than that of the outer phase, the program expects a **normal** pendant drop, in the opposite case, an **upside-down** pendant drop is expected. For sessile drops, the density difference will be of opposite sign. Pendant and sessile **bubbles** will also be treated correctly according to the density difference. *Contact angles will be converted to the complementary angle (180 - θ) if the droplet phase is "Air" or "Gas".*

To save a changed version of the Parameter file, choose Save or, to make a new file, choose Save as. In the latter case, the original file is unchanged. To exit without any changes, choose Close.

Method editor

The Method controls most of the different options for measurements and calculations. This editor window is shown below.

The Method Editor



Data Source

This is a pull-down list that selects from where the experiment takes its data; the value may be either Video or Disk file. The normal mode is Video. If the data source is Disk file, the method is a **Recalculation Method** as described below under "Recalculation".

Data storage

This is also a pull-down list and controls the data storage of the experiment. Normally, the value in this box will be None, and no data will be stored. This also means that the experiment cannot be recalculated later by using a recalculation method. If the value is Profile (dat), the co-ordinates for the profile, found by edge detection, are stored. With the

Bitmap (pic) box checked, a bitmap only picture will be stored for each measurement. The bitmaps will be numbered <name>[0].PIC, <name>[1].PIC ... etc. where <name> is the experiment's (parameter) name (without the < >). If the value is Bitmap (bmp), a full Windows bitmap picture will be stored for each measurement. The pictures will be numbered <name>[0].BMP, <name>[1].BMP... etc. If the value is Bitmap (gif), a full Graphic Interchange Format (GIF) picture will be stored for each measurement. The pictures will be numbered <name>[0].GIF, <name>[1].GIF. etc. If the value is Buffer (raw), the file buffer will be saved with the name <name>.RAW. This format is a sequential file of each picture without any formatting information. The file is uncompressed. Recalculation is possible for all formats, but the same file format must be selected both in the measurement and recalculation methods.

Note: Bitmap storage must be used with care, as one picture takes 300KB or more of disk space and may fill the disk quite fast. A profile data file usually takes less than 6KB. In order to conserve space for bitmaps, the compressed GIF format may be used, but at the cost of slightly longer processing times. This will only have significance with very fast measurements, however (<1 sec). Bitmap storage may have great advantages if used with care. For instance it may be used with pendant drops that may fall off during the experiment, or sessile drops that deform to a great extent, thus making calculations uncertain. By storing bitmap data and simultaneously selecting None for Calculation (see below), pictures are just stored, and a safe recalculation of only the good pictures can be performed later. This may save the experimenter a lot of time and frustration!

By using one of the bitmap storage options, you may also review the experiment later as video sequence, and this may even be converted to a Windows video (AVI) file by an external program.

Report

Selects the type of report produced from the experiment. Time, Gamma, Beta etc. are always written to the screen in the results window. The report is an additional output possibility that is suited for printing, import in word processing documents, etc. The Report field can have the values None, Screen, Printer, or Disk file. With Screen as the option, the report is showed on screen in a separate report window that appears after the experiment is finished. The report window is a small text editor and has its own Main menu and speed buttons by which the report may be saved, printed, etc. With Printer the report is output directly to the default printer (controlled by File | Print setup). With File, the program writes the report directly to a **rich text file** with the same name as the experiment (parameter file) and .RTF extension. This file may be opened directly in a word processing program. It should be noted here that a report is **always** prepared internally by

DROPimage Advanced whatever the value of the Report field. This report may be shown by Results | Show report with the same result as if the Report field was Screen. This means that the Report field is mostly useful for automatic printing and/or saving of reports. Only the report from the most recent experiment is available in this way, in order to save reports automatically, Disk file should be selected. The fields in the report may be selected by the Report | Setup report dialog. The Report editor window and the report setup are described under Reporting and printing data below.

Calculation method

Determines the method used for calculation of the surface tensions. Except if None is selected, the Ratio method is always used to produce initial values and with this option, no further processing is done. The value of Opt in the Surface tension results table will be 0. With the Calculation field set to Contour the initial values are used as start-point in a further optimization step using last squares and second order inter-/extrapolation as described in Appendix A. Only one step is performed here, and Opt=1. This will often be sufficient to obtain more reliable results. If time is not critical for the experiment, Optimized should be chosen. This will let the program perform successive optimizations until a stable value is obtained, or until the number of optimizations reaches the upper limit, Opt_{max}. The maximum allowed relative error, ε, and Opt_{max} are parameters that are read from the system start-up file but may be changed in the Measure | Options window. More details of the calculation method are given in Appendix A.

Data file directory and drive

Selects where the experiment's data files are stored. These are the bitmap and profile-data files, the log-files and report files. It is possible to store data on diskettes by specifying **a:** or **b:**. All the system files, including parameter and method files, are stored in the program's start-up directory, which is selected in the File | File setup dialog (see above). This field must be present.

Type of drop

Selects the "type of drop" to be measured, Pendant drop, Sessile drop or Contact angle. The latter is not really a drop "type", but the 3 options are mutually exclusive. This field must be correct if the program is to give correct results. Pendant and sessile **bubbles** are treated as the corresponding drops, except for the densities (in the parameter file) that are interchanged. This adjustment is made automatically (see above) by the program. The Contact angle option means that the method of geometric extrapolation is used to the timed experiment, thus it is possible to measure time dependent contact angles automatically by this method. If you select

Contact angle, two additional small boxes appear to the right of the text. These contain an L and an R, respectively, or may be empty. The boxes select at which side of the drop the contact angles are measured. Left, right, or both. The L and R are toggled on and off by clicking the corresponding box with the mouse.

Type of measurement

This field selects the type of experiment to be performed, Constant volume, Relaxation/pulse, or Oscillation (the latter is only visible if activated in the Drop.ini file). The Constant volume option gives a "normal" timed measurement and does not require any additional volume control devices (if volume is to be kept constant by the feedback method, the auto syringe is still required). The Relaxation/pulse option allows for more complex measurement procedures, but require additional drop volume control hardware to be installed. This is also the case with the Oscillation option. This type of measurement makes it possible to calculate surface dilatational properties. The special parameters for oscillation experiments are described in the separate paragraph "Oscillation Maeasurements" below. The fields in the group box below the Type of measurement box will change according to which of these two options that are selected, and is therefore suitable to treat these cases separately:

Constant volume parameters

These fields control the timing of the experiment and the number of measurements. The fields, as shown in the figure, are partly self-explanatory. The maximum Number of experiments in a series is theoretically unlimited, and the time is given in seconds. The Initial delay is the delay from the start of the experiment to the first measurement and the Time interval is the interval if equidistant timing is used. If a Time file is used, this field is disabled. The timing of experiments is described below. The Keep constant combo box to the lower right selects if you want to keep the drop volume or the drop area constant by means of the volume control hardware. If this option is selected, the program measures the drop volume *and* area at equal time intervals (the interval is selectable from the Edit | Options dialog) and compares the present value with the initial value. If the change in drop volume is more than the syringe volume step, the volume is adjusted correspondingly (an area change is converted to a volume change). This feature makes it possible to measure at very long times without the usual problems of drop shrinkage.

Timing of experiments

In this program you may use either equidistant time intervals, or so-called **Time files** or **Event files** (which are the same type of files, but with

additional capabilities). A time file is a table of measurement times that determines the timing of experiments; thus any kind of time profile can be used, for instance logarithmic, square root or some other function. The time files are maintained in the **Time file editor**, described below.

Short time intervals

If the time interval between measurements are 0 or at least less than the time the system uses for one measurement (with optional storage and/or calculation), the time interval will be equal to the video speed, i.e. 1/25 s (CCIR) or 1/30 s (US). This timing will be kept if there is enough memory available for all the pictures to be stored in RAM. If there is too little available RAM, the operating system will use virtual memory (the swap file on the hard disk) and the time will increase.

If the capture time is less than what the system uses for one calculation (this time is system dependent and is set in the initialization file) the program will delay calculation until there is a time interval where one or more of the captured pictures can be calculated.

The pictures will always be calculated in the correct sequence, starting with 1. The program will automatically determine how many images that must be captured before calculation is started. The left field of the status bar at bottom of the main window will indicate the present program operation (for instance which picture number is being captured).

Time and Event files

If Time file or Event file is checked, the Time/event file group box is active. To select a **Time file**, either enter the file name, or click the Get file name button to open a dialog box to select the file. The entries in the time file will then determine the times for each measurement instead of a fixed time interval. The delay time will be the first entry in the file, and the file must contain sufficient entries for all the measurements. The time entries may be spaced in whatever way you like, and may facilitate logarithmic, power or other non-linear time scales. The generation and editing of the time files is described in section "Time file editor" below. The Time files are a very flexible way of controlling the timing of experiments, and any method may use any time file. The time files are ordinary text files with one time per line and may therefore be produced by other programs (for instance spreadsheet programs or text editors). They must have the extension .TIM.

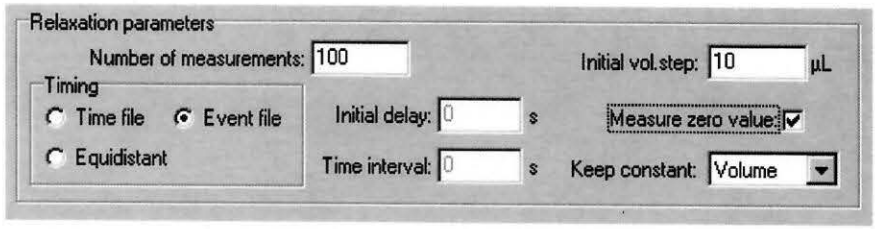
An **Event file** contains the same information as the time file, plus some additional functionality in the form of three extra entries per time value.

These entries are used when the Relaxation/pulse type of measurement is selected. The extra entries are the Volume and Measure fields. In addition there may be an additional Comment field. Se the description of the Event file editor below. You may use a time file in a Relaxation/pulse experiment without the additional fields. Then the Volume field is set to 0 and the Measure field to 1, corresponding to a constant volume experiment. The methods are then equal except for the initial volume step (if this is 0 the methods are equal).

Relaxation/pulse parameters

The fields are equal to those for Constant volume except for two additional fields, the Initial vol.step field and the Measure zero value checkbox. The group box is shown in below.

Relaxation parameters in the Method editor



The initial volume step is taken immediately after the start of the experiment. The zero value measurement is taken before this volume step. If the drop is too small or absent at this time, the Measure zero value box should be unchecked, else the program may stop. If Volume or Area is selected in the Keep constant combo box, the volume or surface area will be kept at the value measured after the initial step (after the Timing interval in Edit | Options).

This will counteract possible later intentional volume changes set in the event file, and this option should therefore be unchecked if timed volume changes are to be used.

Use of Event files

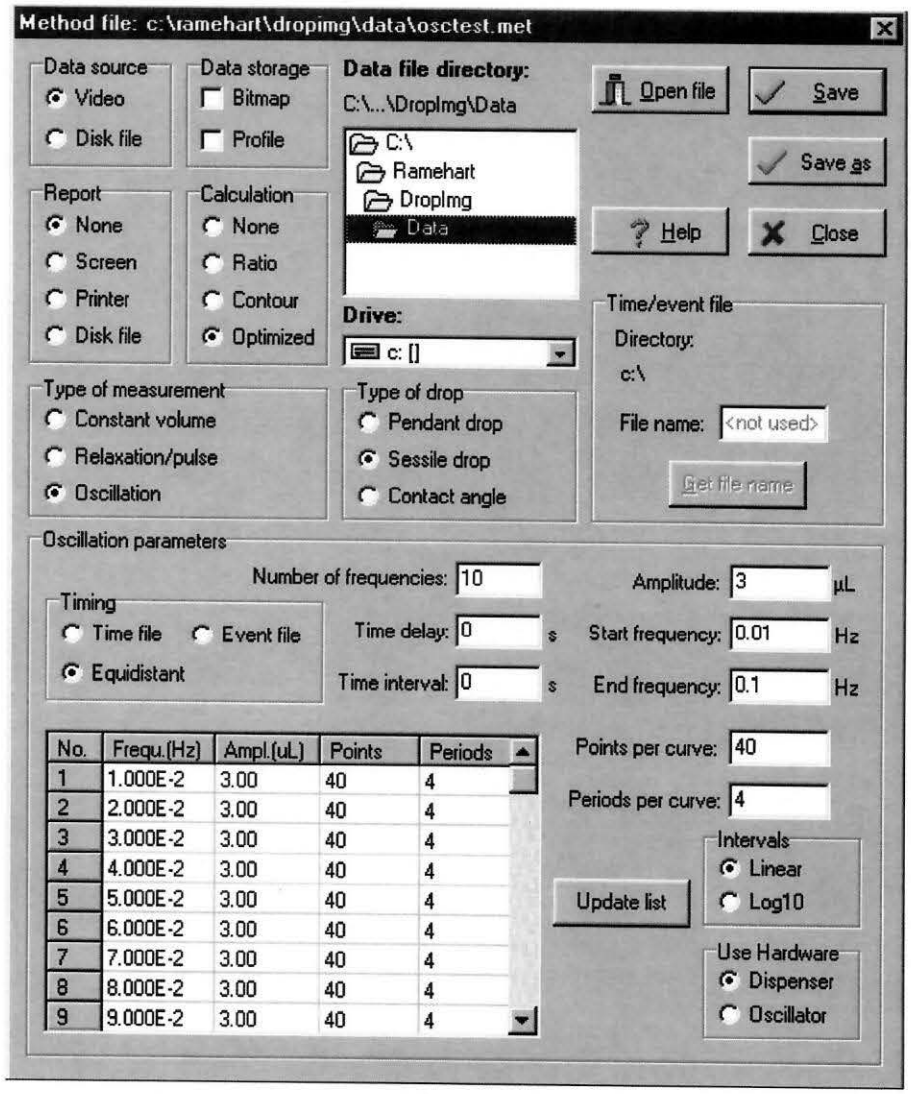
As mentioned under Time files, the event files also determine the timing of the measurements. However, in addition to the time values, the two extra fields, the Volume and Measure fields may be used to control volume steps and measurements. The Volume field gives the volume step (in mm^3) taken at that time, and the Measure field, which is "N" or "Y" determines if a measurement is taken at that instant, right after the volume step. An event file may therefore be constructed to make many types of pulsed

experiments, even slow oscillations are possible by using the sine volume function (included in the Editor, see below).

Methods for oscillation experiments

When the Oscillation button is selected, the size of the Method Editor window will expand downwards, as seen below. The Number of measurements box will be renamed to Number of frequencies, in addition to the other 3 boxes on the right hand side, named Amplitude, Start frequency and End frequency. In addition, new boxes appear together with the frequency list table. Most fields, including the table, are saved with the Method.

The Method Editor when Oscillation Is selected



The oscillation experiments are controlled by the elements in the frequency list table. The values in the 5 edit boxes to the right, together with the Intervals group, are used to generate the frequency list. The list always takes precedence if the values of the edit boxes are changed without generating a new list, or if the list table is edited by hand. This means that it is possible to vary the frequency, amplitude, and number of points and number of periods individually for each experiment.

To make a new frequency list, fill in the Number of frequencies, Amplitude etc. and hit the Update list button. The generated list may then be edited by hand and the method saved. DROPimage will read the list when a new oscillation experiment is started.

The values of the Timing group have no influence on the oscillation experiment, except for Time delay and Time interval. The Time delay in this connection is inserted before each oscillation measurement series is started. It may or may not have much significance. The Time interval will be used as the interval between separate frequency runs when a series is run automatically.

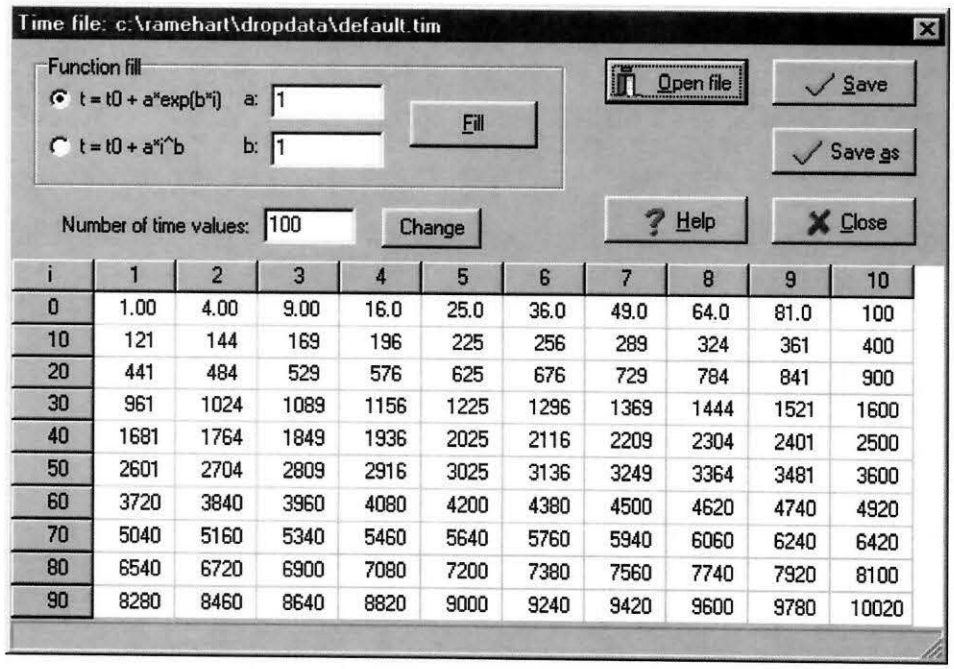
The use Hardware

Time file editor

The Time File editor is used to edit the timing of the measurements in an experiment and is shown below. The timing table has rows of 10 columns each that contain the time values for an experiment. A time file also can contain any number of values, and if the number is not an order of 10, the remaining cells will be 0. At the top of the window, there is a group box for Function fill and at the bottom is the Status line that lists the number of time values in the file. You may move around in the time table by means of the arrow keys or the mouse, and enter new values in any cell.

The time values in the file are integer values, either in **seconds**, **minutes or hours**. If in minutes, the number has an **m** (lower case) as label after the number, if in hours, the label is **h**. Time values may be entered in either of these formats, i.e. times in seconds are entered as integer numbers and in minutes or hours as integer numbers followed by an **m** or **h** (no space). Other labels will not be accepted when you try to save the file, and in that case no change will be saved.

The Time file Editor



i	1	2	3	4	5	6	7	8	9	10
0	1.00	4.00	9.00	16.0	25.0	36.0	49.0	64.0	81.0	100
10	121	144	169	196	225	256	289	324	361	400
20	441	484	529	576	625	676	729	784	841	900
30	961	1024	1089	1156	1225	1296	1369	1444	1521	1600
40	1681	1764	1849	1936	2025	2116	2209	2304	2401	2500
50	2601	2704	2809	2916	3025	3136	3249	3364	3481	3600
60	3720	3840	3960	4080	4200	4380	4500	4620	4740	4920
70	5040	5160	5340	5460	5640	5760	5940	6060	6240	6420
80	6540	6720	6900	7080	7200	7380	7560	7740	7920	8100
90	8280	8460	8640	8820	9000	9240	9420	9600	9780	10020

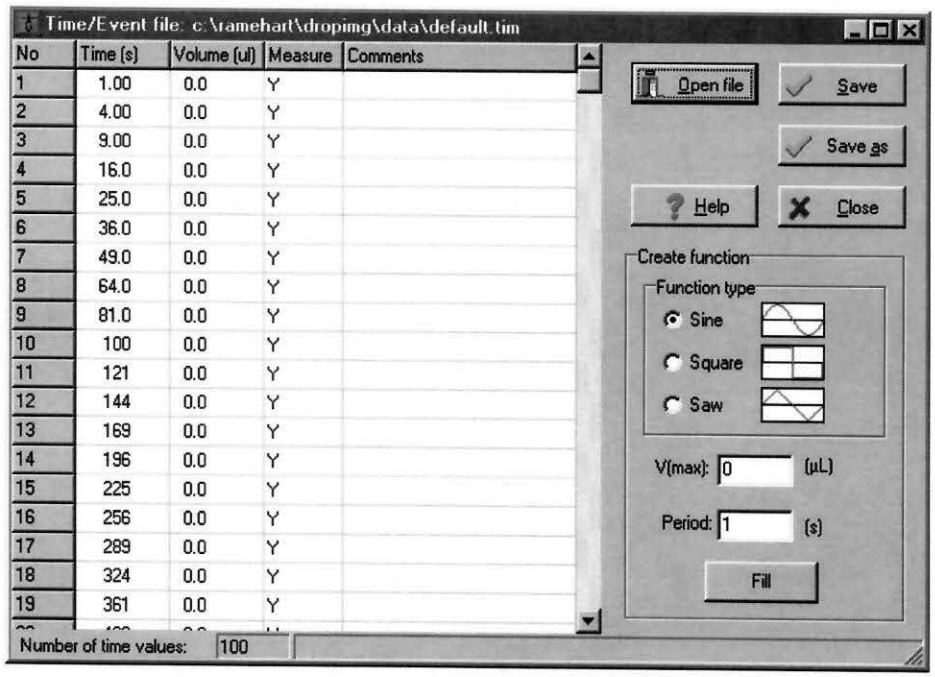
The Number of time values box determines how many values the file will contain. If you want to change the number, enter a new number, and press the Change button. The table will then expand or contract to facilitate the new number. The number of columns will always be 10. If necessary, a scroll bar will appear at the right margin.

As indicated in the Function fill group box, the two functions may be used to fill the screen with calculated values in order to give a suitable non-linear scale. Only the values themselves are saved, and they may also be edited after a fill operation. The two functions available are an exponential function (which gives a "logarithmic" scale) and a power function. The start address for the function fill is at the cursor position and the value of the start time t_0 will be the value **below** this cell (0 if the cursor is at the first cell). When choosing one of the functions, the two constants **a** and **b**, which can be any integer or decimal number, are used for the calculation of time values. The value of **i** is the cell index. The calculated times will be rounded to the nearest integer. When you are finished editing, save the time under the same name by choosing Save or a new name by choosing Save as.

Event file editor

The Event File editor is somewhat similar in function to the time file editor, but still different. The editor window is shown below.

The Event file editor



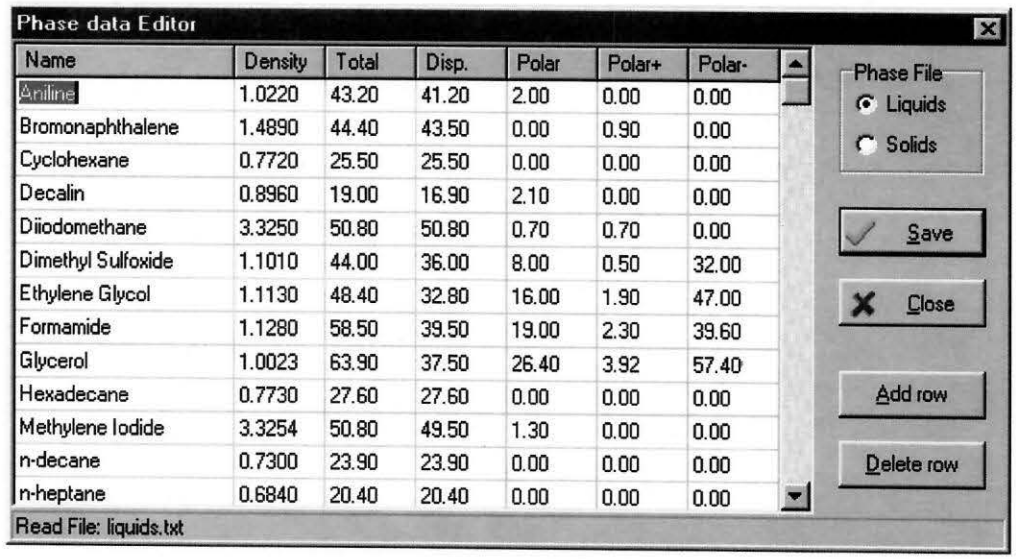
As mentioned above under Timing of experiments, these two editors operate on the same files, with extension .TIM. However, in the Event editor all the fields in the file may be changed, while the Time editor only changes the first column. Also a time/event file may have 1 to 4 values per line, the difference lays in the way the files are used. A constant volume experiment only uses the first value, the Time, while a Relaxation/pulse experiment uses 3 values, Time, Volume and Measure. The Volume parameter tells the program to change the volume from any initial value at the given time, and the Measure parameter determines if a measurement is to be taken immediately after the volume change. The Comment parameter is optional and has no function in the program.

The Fill function in the Event editor will fill the Volume column, and not the Time column, as in the Time editor. The point with filling the volume column is to help making functional changes of the drop volume, for instance a sinusoidal oscillation, a square pulse or a saw pulse. These three functions are available in the Function type group. The parameters that control the created volume data are V_{max}, the volume amplitude (in microliters) and the Period (in seconds). The Square function will produce a square pulse, with the given period and volume amplitude, and the saw function will make a sawtooth wave, also with the same frequency and amplitude. The pictures adjacent to the buttons illustrate the type of function form created. You may also of course edit all volume values manually. In order to toggle the Measure field between "Y" and "N", click the **right** mouse button over the field.
The Event editor cannot change the number of time and volume values in the file, use the Time editor for this.

Phase editor

In order to maintain the two files liquids.txt and solids.txt that are used in the list boxes in the Parameter editor, the Phase editor is convenient.

The Phase editor

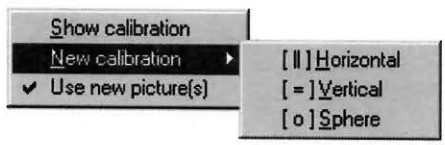


The function of this editor is mostly self-explanatory. The Name field may contain up to 255 characters. Total is the total surface tension of the liquid, while Disp. and Polar are the dispersive and polar components of Total. The Polar+ and Polar- values refer to the acidic and basic components of the non-Lifshitz-Van der Waals components, according to the theory by van Oss and coworkers. The sequence of substances is the same as in the file, i.e. the data are not sorted.

The files should not be edited in an ordinary text editor (such as Notepad) in order to avoid formatting errors, but may be imported to and edited in a spreadsheet program, as for instance Excel.

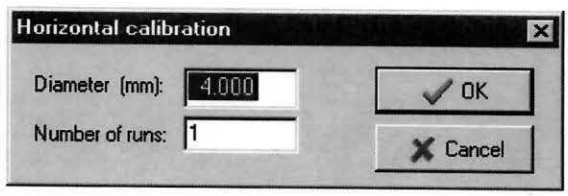
CALIBRATING THE SYSTEM

In order to calculate correct surface tensions, the magnification of the video picture must be known. By calibration, the program measures a known object, and the size of the pixels in the vertical and horizontal direction is calculated automatically. The calibration procedure must be performed every time the magnification of the optical system is changed. When DROPimage is started the last calibration is automatically restored (this is stored in the file DROP.CAL). Measuring the diameter of a cylinder placed in the camera's view usually performs calibration. As cylinder, a steel or glass rod or a tube may be used. This object must be measured accurately by some other method (for instance a micrometer gauge). The Calibration menu contains three lines, Show calibration, New calibration, and Use new picture(s)/Use present picture. The latter is a switch that will flip every time it is selected. The **Show calibration** menu option just shows the Calibration values window. The **New calibration** option has a submenu, as indicated by the arrow:



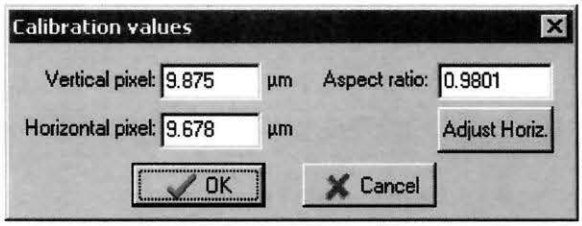
[||] Horizontal means that the (horizontal) width of a vertical cylinder is measured, and [=] Vertical is the opposite of this. The [o] Sphere calibration is intended for measuring a spherical object, freely visible in the picture. When one of the submenu options is selected, the calibration start dialog is displayed; the heading varies with the type of calibration. The dialog for Horizontal calibration is shown below:

The Horizontal Calibration dialog



The Diameter is the size of the object and the value is taken from the initiation file. Another value may be entered, and a Number of runs may be selected for an even better accuracy. When the OK button is clicked, the number of runs is measured and an average value from all the runs is used for calculation of the pixel size. The result is presented in the calibration value window.

The Calibration window



In a **horizontal** calibration the horizontal pixel size is measured and the vertical pixel size is calculated from this value and the aspect ratio. In a **vertical** calibration, the opposite procedure is used. Vertical calibration should be used every time the magnification is changed, and is therefore the "ordinary" type of calibration. The start window for horizontal calibration is similar to that for vertical calibration.

In a **sphere** calibration both pixel sizes and the aspect ratio are calculated, so this may seem as the best method for calibration. The whole sphere must be visible in the picture, and no disturbances must be present along the sphere surface (no suspending wire or other surface). Also for this function, the default sphere diameter is taken from the initiation file. The program will determine the complete profile of the sphere, and calculate the vertical (x) pixel, horizontal (y) pixel and aspect ratio (y/x) from 2nd degree polynomials fitted to the 4 extreme regions (upper, lower, left, right). However, experience has shown that the aspect ratio calculated by a sphere calibration may not be the best in all situations; therefore it is possible to make small adjustments of this ratio manually. The best value is usually found when the surface tension does not change with drop size, and a pendant and sessile drop of the same liquid gives the same surface tension (this may still not be obtainable in all situations, from different reasons).

The Use new picture(s)/Use old picture switch selects if calibration is done on (a) new picture(s) from the frame grabber, or on the picture already shown. The former case will be normal (default), while using the picture shown allows for calibration from saved pictures (all supported formats). This makes it possible to calculate experiments done with another system, if a calibration image is available for that system.

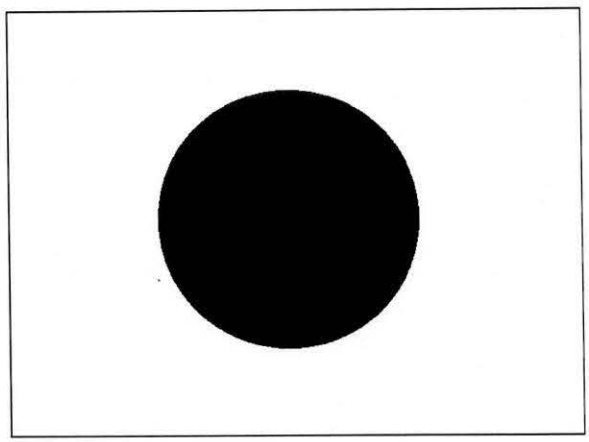
A first time calibration of a new system should be performed by a Sphere Calibration, as it is necessary that the aspect ratio be calibrated, as well as the magnification. This calibration should also be done if ever the camera and/or the frame grabber board are changed, because small differences may exist between models. Usually, this calibration is done from the factory when DROPimage is installed on a new system.

If ever changing the optics of the imaging system so that the magnification is changed, the Sphere Calibration may be repeated, or the more simple Horizontal Calibration may be used.

How to perform a calibration

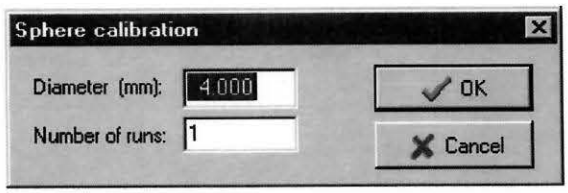
Sphere Calibration

To perform the Sphere Calibration, use the sphere calibration tool, which is a steel ball bearing glued to a glass slide. The glass slide is mounted vertically, so that the steel ball is imaged through the glass, and is positioned in the middle of the picture, as shown below.

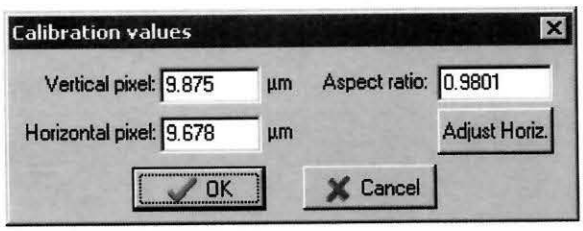


Pull down the *Calibration* Menu, choose *New calibration* and then *Sphere.*

You will see the picture of the sphere is the Main window, and the Sphere calibration dialog box as shown above.



The *Diameter* is the size of the sphere taken from the initiation file. If the size if different, you may enter another number. The *Number of runs* may be selected for better accuracy, but often 1 is sufficient. Click the OK button and the number of runs are performed and the vertical and horizontal pixel size and the aspect ratio are calculated. The result is presented in the calibration value window shown below.

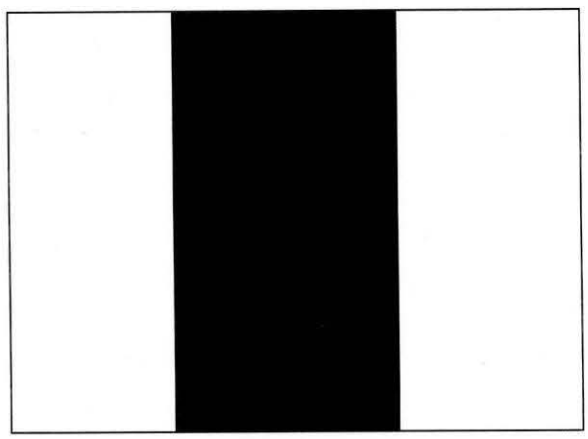


Because both the video camera and the frame grabber board have "square pixels", the aspect ratio will be close to 1.0, but will often differ slightly because of small inaccuracies in the hardware. Correcting for this deviation will often be important in order to obtain accurate surface tension readings

Click OK and the measured values are stored in the DROP.CAL file.

Horizontal Calibration

To perform the Horizontal Calibration, use an even metal tube or metal rod. Do not use a glass tube or glass rod. The rod is mounted vertically and positioned in the middle of the picture, as shown below. There must be ample room at both sides of the rod, and no room at the top or bottom, as shown in this picture.



Pull down the *Calibration* Menu, choose *New calibration*, then *Horizontal*. You will see the picture of the rod is the Main window, and the dialog box as shown above. The *Diameter* is the diameter of the rod taken from the initiation file. If the size if different, you may enter another number. The *Number of runs* may be selected for better accuracy, but often 1 is sufficient. Click the OK button and the number of runs is performed and the horizontal pixel size is measured. The vertical pixel size is calculated from the aspect ratio. The result is presented again in the Calibration values window. Click OK, and the measured values are stored in the DROP.CAL file.

Note that this procedure does not alter the aspect ratio.

WORKING WITH DROPIMAGE FILES

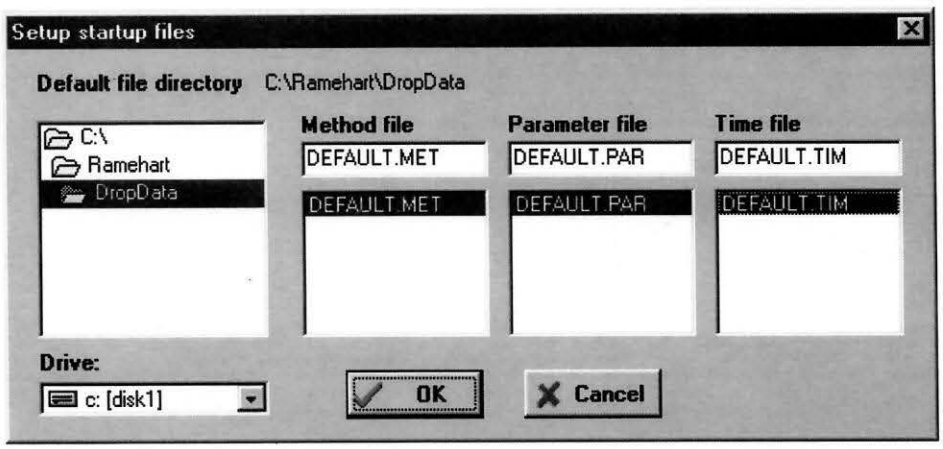
Most file operations in DROPimage are handled automatically by the measurement procedures. However, file handling is also available from the menu system. The **File menu** consists of functions to open and save bitmap pictures and profile data files and to the **File setup** dialog. In addition the **Contact Angle File Control** is available from the File menu, in addition to being available from all the tools. The **Results menu** contains options for the loading, saving and printing of **reports**. Also the Report window has its own menu with similar functions.

File setup

The default startup file directory and startup method, parameter and time files are read from the initialization file (**drop.ini**). They may be changed by using the File | File setup dialog shown below.

The startup files must be in the Default file directory. When running an experiment, the location of the Method file is determined by the Method setting in the Parameter file (see Parameter editor), and the Time file by the Time file setting in the Method file. The default files are therefore startup files only. The Default file directory however, will be used throughout the program for file dialogs.

File setup dialog



Opening a picture

The File | Open picture function restores a bitmap file that was formerly saved by a File | Save picture function or by a timed measurement with Bitmap storage selected in the Method.

The speed button  has the same function as the File | Open picture function.

The supported file types are:

PIC Uncompressed bitmap only, one byte per pixel and no header data. This is the same format as the files that the program saves when the Data storage field in the Method is Bitmap. The value of * must be a number.

BMP Windows Bitmap format (uncompressed). The bitmap data is the same as in the PIC files.

GIF Graphic Interchange Format (CompuServe). This is a compressed format and the bitmap data usually takes less space than the other formats. The disadvantage is that compression/decompression takes some time, but with a fast processor this is hardly noticeable.

A PIC bitmap picture is read into memory and displayed on the screen in the picture window. It may then be further processed by filtering etc. A BMP or GIF file is also converted to the internal format and may be processed in the same way. This means that DROPimage is able to read BMP and GIF files created by other programs; however these files cannot be very much larger than the pictures generated by the program. DROPimage cannot read TIF-files.

Saving a pictures

The File | Save picture function saves the bitmap in the memory buffer to a disk file.

Also the speed button  has the same function.

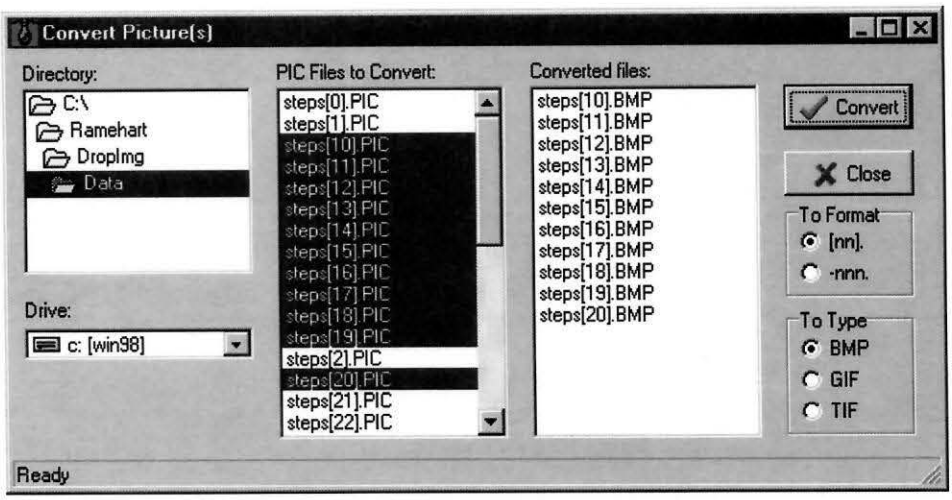
The supported file types are those described under Open picture, plus the TIFF file format:

TIF TIFF (Tagged Image File Format) format (uncompressed). The bitmap data are the same as in the PIC files, but the file header conforms to the TIFF data format.

Files saved in the BMP, GIF or TIF formats may be read by other programs, This is a convenient way to export pictures for printing, editing etc. The pictures are in 8 bit black & white format (256 grays).

Converting picture files

Native bitmap files (PIC) may be converted to the other bitmap formats in one operation through the Convert file(s) dialog on the File menu. When selecting this option, the dialog window as shown below is opened

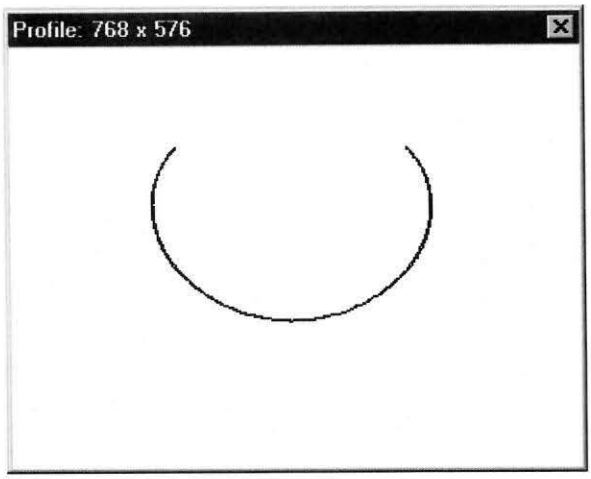


When a drive and directory is selected, all PIC-files in that directory are listed in the PIC Files to Convert box. One or more of these files may be selected for conversion in the usual way and then converted to the desired format in one operation by clicking the Convert button. The format is selected by the To Type radio group and the format by the To Format group. The first format, [nn], is DROPimage's own format and should be used if the files are to be used further in DROPimage (for instance by Recalculation). The second format (-nnn) is used by some application (for instance Adobe Premiere) to convert a sequence of single bitmaps to an animated GIF, video file (AVI) etc. The converted files are shown in the right box, **after** conversion. This box does not list files of the To Types that are already in the present directory.

Opening a profile-data file

If Profile (dat) is selected under Data storage in the Method, the profile data are saved by the measure procedures as file with the name <name>[nn].DAT where <name> is the experiment's name (parameter file) and nn is the picture number. These profile files may be read back into the program by the File|Open profile-data file function and will then be plotted in a window like that shown below. The numbers in the title bar shows the size of the bitmap from which the profile has been determined.

Plot of Profile data



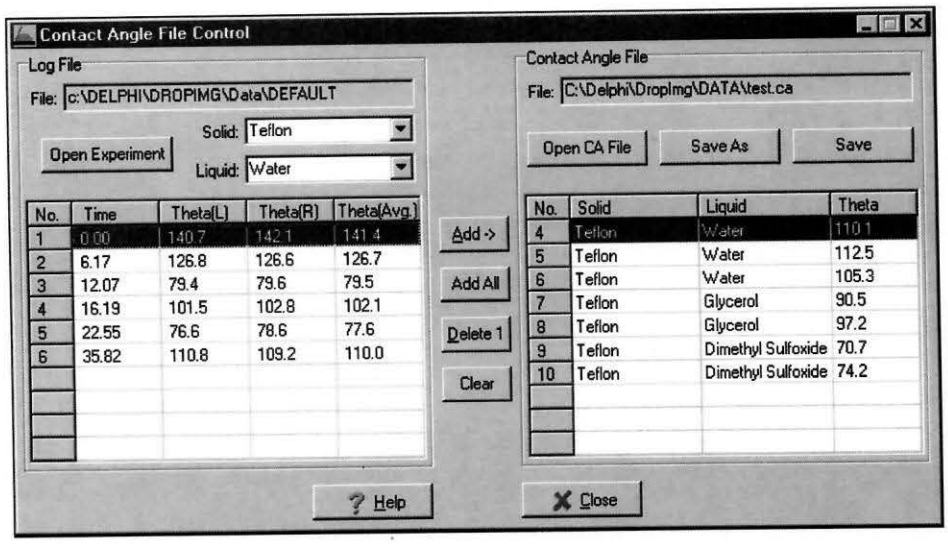
Saving a profile-data file

The File | Save profile-data file function saves the profile-data, either to a standard profile file (type DAT) or to a text file (type TXT). The text file does not contain information on the size of the original picture or some other key data in the same way as the standard profile file. These files are only intended for data export, and cannot be read back into DROPimage.

Contact Angle File Control

The Contact Angle File Control (**CAFC**) is the interface between DROPimage's contact angle results and the different **Surface Energy Tools**. These tools read contact angle data from Contact Angle (**CA**) files that contain information on the type of solid and liquid(s) involved, contact angles, and interfacial tensions, when needed.

DROPimage measures contact angles either in Method-driven sessile or pendant drop interfacial tension measurements, in Method-driven contact angle measurements, or by the Contact Nagle tool. The Method-driven results are saved in log-files (of type *.log) and the CAFC will read these log-files and produce CA Files. The CAFC is very flexible and makes it possible to incorporate CA measurements from different runs in one CA file. It is also possible to **read** and **merge** CA files, as well as **add** and **delete** records from CA files.



The **Left pane** contains the data in the **Log File**. At program startup, the data will be those in the Default.log file. The **Solid** and **Liquid** names are taken from the corresponding experiment (the data in the Parameter file with the same name as the log file, without sequence numbers (in this case, the Default.par file). You may open other Log Files in this pane, the new data will replace the old. The data shown is from a timed contact angle experiment. If the experiment is a surface tension experiment, the columns will contain Time, Gamma and Theta.

You may change the Solid and Liquid names if they are wrong by preferably using the pull-down combo boxes. The names in these boxes are those in the Solids.txt and Liquids.txt files. These names may be changed in the Phase Editor.

The **Right pane** contains the data in the **CA File**. These are Live Data that are immediately available for use in the Solid Surface Energy Tools. The **Open CA File menu** options in these tools have the same function as the **Open CA File** button in the Right pane. When a new file is opened, the data are **appended** to the live data and the right table.

When using the Surface Energy tools, it is important to be aware of the "live" connection between the contact angle data that are used. All tools and the CAFC use the same live data. These data are those visible in the right pane of the CAFC and also in the Contact Angle (CA) tool window. The content in these two windows is synchronized. Changes to these data from the CAFC or any of the tools will affect the data available to all other units. This means hitting Clear in the CAFC, CA tool or Reset in any other tool, clears the live data from all units. In the same way, opening a CA file from any unit, effects the data available to all the others.

The buttons between the panes will add records from the left table to the right, or delete lines in the right table. The **Add** button will add those lines that are selected (one or more). You can select **consecutive** lines by holding down the <**Shift**> button when clicking the lines. You cannot select non-consecutive lines. The Delete button deletes the selected lines in the right table (one or more).

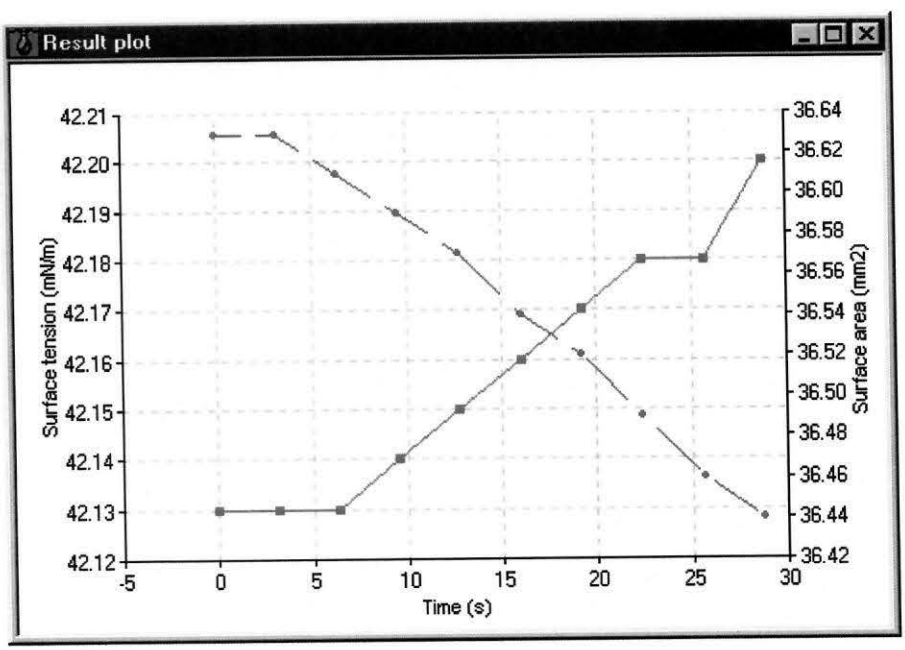
Saving a Report

The last report produced by the measurement procedure, or loaded by the Results | Load report function may be saved either by the Results | Save report function or by the File | Save function in the Report window menu. The report will always be saved as a Rich Text File (RTF). As such, formatting, tabs, etc is saved with the file.

PLOTTING DATA

DROPimage does not have extensive graphing functionality, as it is felt that this in not necessary (or desirable) in a Windows program. By using the LOG files automatically produced by the program, report files, or the Windows clipboard, data may easily be copied into specialized graphing programs. DROPimage does have a quite useful **graph window**, however, that may be switched on before starting a measurement (it will then stay on until switched off), or plot the results after the experiment is finished.

The Graph window



The Graph window

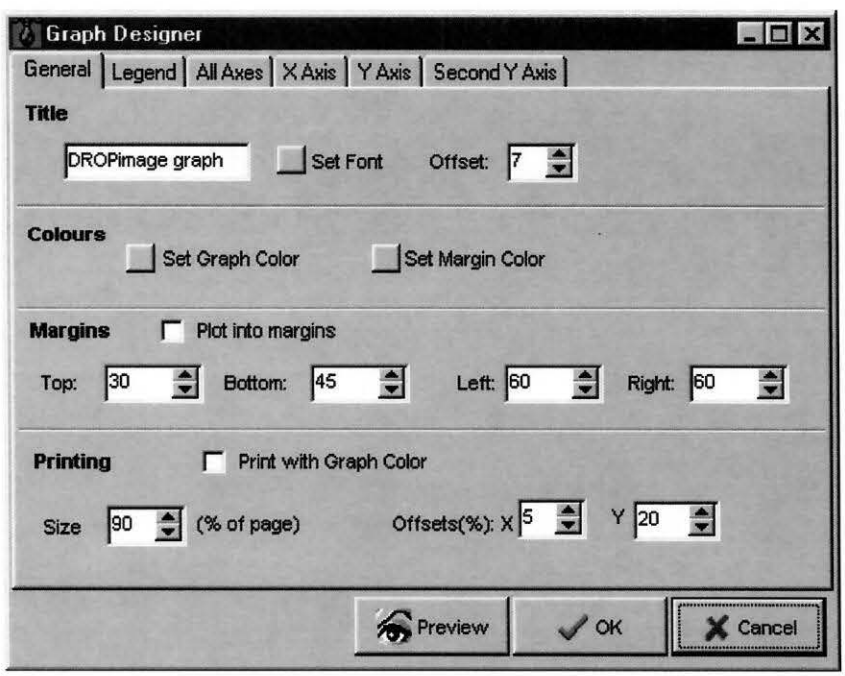
The graph window is initially switched off, and is turned on by the Results | Show graph function. To select automatic graphing of results the Continuos results plot checkbox in the Options window that is selected by the Measure | Options function (see the chapter on Options below). The graph window can show one or two graphs at the same time. The x-axis represents the time, and the (two) y-axis may be selected among the 5 results in the Results notebook. The graphs are **auto-scaled**; meaning that all the data will be shown at any time. The scale will change dynamically during measurements to include all new data. The graph window is **sizable** and may be maximized and minimized, the graph will always be fitted to fill the whole window. The scale may be changed manually in the Graph Designer (see below).

The graph may be **copied** to the Windows clipboard by selecting Results | Copy graph when the graph window is visible. The graph may then be pasted in other Windows applications, for instance word processors or graphics programs.

The Graph Designer

Many properties of the graph(s) may be **customized** in the **Graph Designer**. This window will appear by selecting Results | Graph Designer or by double-clicking the graph window. The Graph Designer is shown below.

The Graph Designer window



Many properties of the graph may be customized using the Designer. The 6 different dialog pages are selected by the tabs at the top. The pages are mostly self-explanatory. By using the Preview button, you may view the changes before they are saved. Press the Preview button again to return to ordinary view.

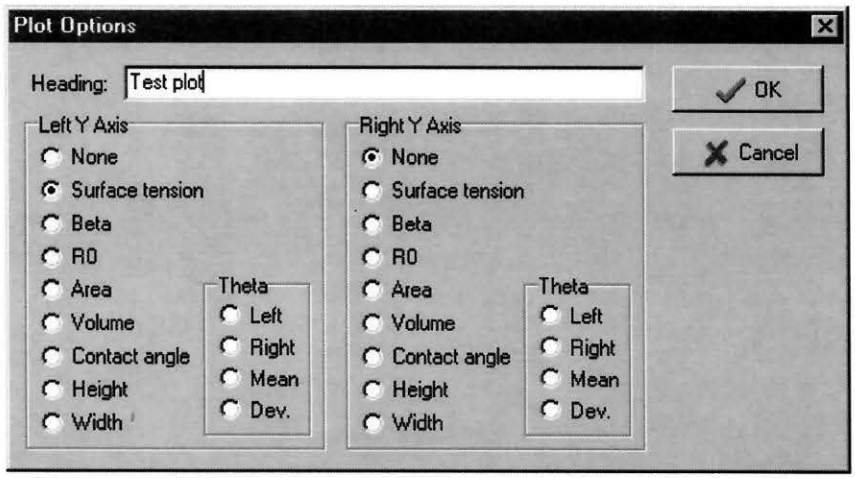
The Graph Control and Graph Designer are copyright © Kestral Computing. For further help on this component, please refer to http://www.kestral.com.au.

Plot options

The variables to be plotted are selected in the Plot options window. You get to this window by the Results | Plot options function. To graph results that are already measured, use the Results | Plot results function. The Plot options window will then be shown first in order to select the variables to be plotted. The window is shown below.

The two radio button groups selects the variables for the left and right y-axis, respectively. The Theta groups select variables for contact angle plots. The Heading box will initially be filled with the name of the experiment (PAR file), but may be changed to something better. The plot options will stay in effect until other options are selected.

The Plot options window



Zoom

The graph window has a zoom function: By holding down the <Shift> key and clicking one corner of the rectangle that you want to magnify, a **cross** cursor will appear. Then while holding down the left mouse button, drag the cross to the other corner and release the mouse button then the <Shift> key. While dragging, a

rectangle will appear, and when the mouse is released, the graph will be re-scaled to show only the points inside the rectangle. If you want to return to the original scaling, hold down the <Shift> key and click the graph once.

REPORTING AND PRINTING DATA

Often results will be exported to other programs for further treatment such as plotting, analysis and printing. In order to make advanced reports, data should be exported to an external program (as for instance a word processor) and formatted in its final form there. However, DROPimage contains some abilities to edit and print results, such as reports and graphs, end in order to get printout of the essential results, the built-in functions are sufficient.

Setting up the printer

The print functions of DROPimage use the standard Windows printing facilities. To select a printer and set up the printer, use the File | Print setup function. The standard printer setup dialog window is shown (this is a standard Windows dialog whose text is dependent on the language of the Windows installation)

Setting up a report

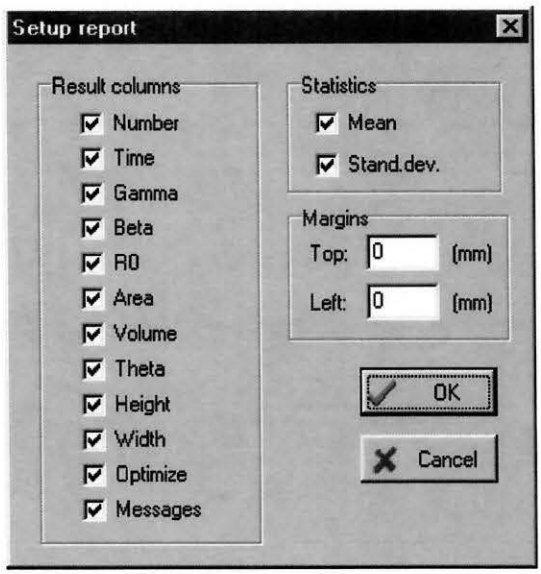
You may select what fields are to be printed in the report by the Results | Setup report function. The following columns are available.

No.	Measurement number
Time	Time from start (seconds)
Gamma	The surface or interfacial tension, g (mN/m)
Beta	The shape factor, β
R0	The radius of curvature at the drop's apex (mm)
Area	The drop surface area (mm^2)
Volume	The drop volume (mm^3)
Theta	The contact angle at the drop limit (horizontal) hairline (deg)
Height	The total measured height from hairline to apex (mm)
Width	The maximum width = the diameter if Theta ≥ 90° (mm)
Opt	The number of optimizations performed
Messages	Errors or other program messages

You may also choose if the mean and/or standard deviation should be calculated and printed as the two last rows.

Mean	The mean of each column except No. and Time.
Stand.dev.	The (sample) standard deviation of each column, except No. and Time.

The Setup report window is shown below. The selected columns will be included in the report in the shown sequence. This sequence cannot be changed.



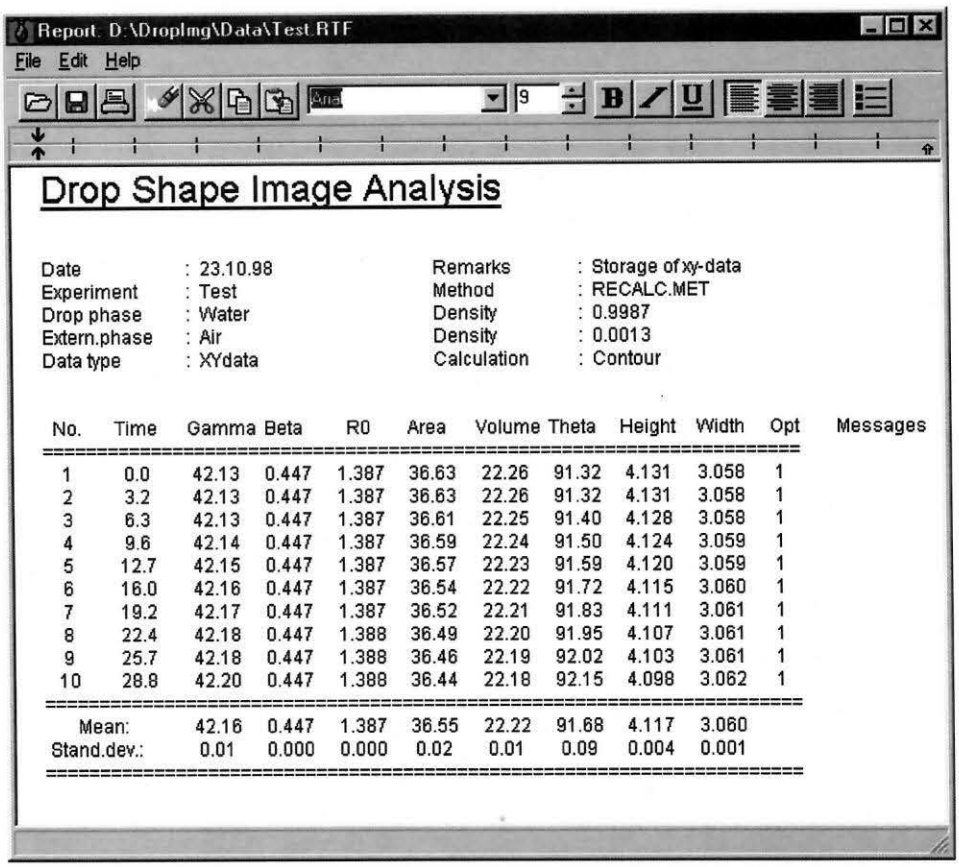
Editing and printing a report

As mentioned under the measurement section, the results may be printed automatically when an experiment is finished by selecting Printer in the Method. To print the report afterwards, use the Results | Print report function or the Print function in the **Report editor**. This editor is used whenever a report is viewed on screen. If Screen is selected in the Report group in the Method, the report window appears automatically when the experiment is finished. Otherwise, selecting Results | Show report shows the report window on the main menu. The report editor window is shown below.

The report will be printed using the current fonts in the report window. The fonts may be changed with the Edit | Font function or by means of the font dropdown list and size spin edit box. The font will either be changed at the insertion point, or in the case some text is selected, will be applied to the selected text. The report editor has cut and paste and even drag and drop functionality. Files are saved as formatted **rich text files**.

When printing from the Report editor, the default printer will be used.

The Report editor window



No.	Time	Gamma	Beta	R0	Area	Volume	Theta	Height	Width	Opt	Messages
1	0.0	42.13	0.447	1.387	36.63	22.26	91.32	4.131	3.058	1	
2	3.2	42.13	0.447	1.387	36.63	22.26	91.32	4.131	3.058	1	
3	6.3	42.13	0.447	1.387	36.61	22.25	91.40	4.128	3.058	1	
4	9.6	42.14	0.447	1.387	36.59	22.24	91.50	4.124	3.059	1	
5	12.7	42.15	0.447	1.387	36.57	22.23	91.59	4.120	3.059	1	
6	16.0	42.16	0.447	1.387	36.54	22.22	91.72	4.115	3.060	1	
7	19.2	42.17	0.447	1.387	36.52	22.21	91.83	4.111	3.061	1	
8	22.4	42.18	0.447	1.388	36.49	22.20	91.95	4.107	3.061	1	
9	25.7	42.18	0.447	1.388	36.46	22.19	92.02	4.103	3.061	1	
10	28.8	42.20	0.447	1.388	36.44	22.18	92.15	4.098	3.062	1	
Mean:		42.16	0.447	1.387	36.55	22.22	91.68	4.117	3.060		
Stand.dev.:		0.01	0.000	0.000	0.02	0.01	0.09	0.004	0.001		

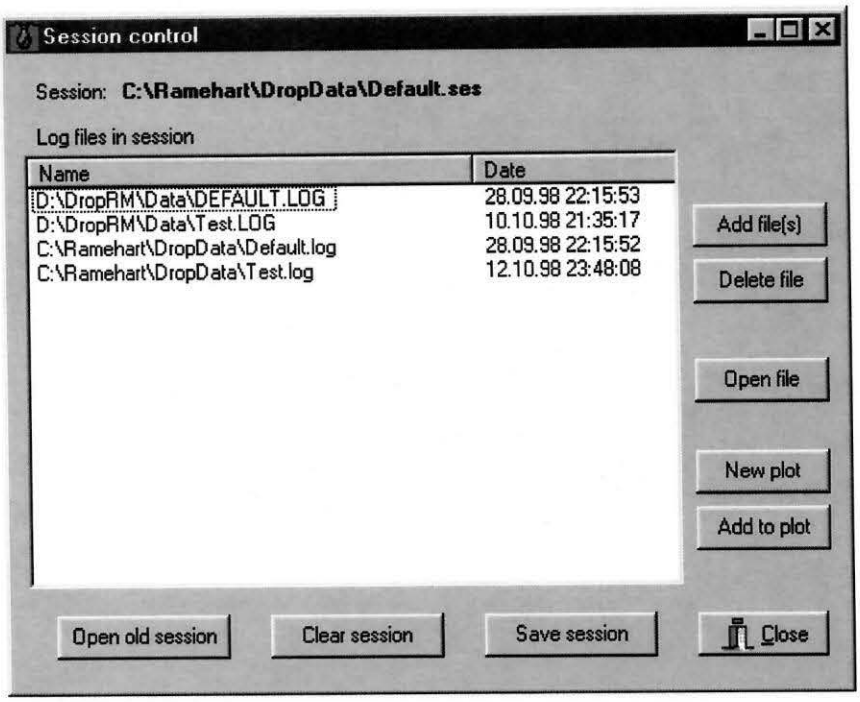
Printing graphs

The graphs plotted in the graph window may also be printed by using the Results | Print graph function. The graph will appear as shown on the screen.

SESSION CONTROL

The Session control function is available on the File menu. With this control you can view, edit and plot log-files from the present program session or from former sessions. You can also add and delete log-files and make special session files as a wrapper for a series of experiments. This window is shown below.

The Session control window



DROPimage will automatically add all new log-files to the present session. The program will always start with the default session (DEFAULT.SES), but you may open another session by using the Open old session button. The DEFAULT.SES file will not be erased at program exit, and can therefore become very long. It may therefore be an advantage to clean up this file at regular intervals by for instance saving it under a new name and/or erasing it.

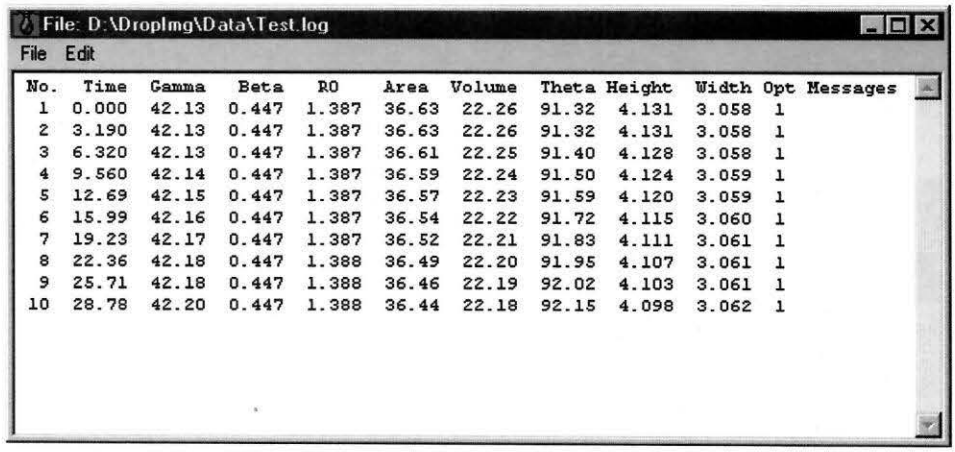
The Add file(s) and Delete file buttons are self-explanatory. As written, it is possible to add more than one file at once from the multi-select file dialog that will appear. Only one file may be deleted at a time. The Open file button will open the log-file in an editor window. From this window, it is possible to edit the log-file. An editor window is shown below.

The Log-file editor looks much like the Report window. It is possible to save the file under a new name and to cut and paste. This may be convenient to for instance remove or correct measurements that for some reason (for instance a bad image) did not give "nice" results. You may also cut to and paste from other applications (for instance Excel).

The two plot buttons are convenient to visualize old results. You may both open a new plot by the New plot button, or add a new log-file to the present plot with the Add to plot button. In this way it is easy to compare different runs. The plot

window and format is the same as described under Plotting data above. The plot options selected from the Results menu are used also in these plots.

The Log-file editor opened from the Session control



No.	Time	Gamma	Beta	RO	Area	Volume	Theta	Height	Width	Opt	Messages
1	0.000	42.13	0.447	1.387	36.63	22.26	91.32	4.131	3.058	1	
2	3.190	42.13	0.447	1.387	36.63	22.26	91.32	4.131	3.058	1	
3	6.320	42.13	0.447	1.387	36.61	22.25	91.40	4.128	3.058	1	
4	9.560	42.14	0.447	1.387	36.59	22.24	91.50	4.124	3.059	1	
5	12.69	42.15	0.447	1.387	36.57	22.23	91.59	4.120	3.059	1	
6	15.99	42.16	0.447	1.387	36.54	22.22	91.72	4.115	3.060	1	
7	19.23	42.17	0.447	1.387	36.52	22.21	91.83	4.111	3.061	1	
8	22.36	42.18	0.447	1.388	36.49	22.20	91.95	4.107	3.061	1	
9	25.71	42.18	0.447	1.388	36.46	22.19	92.02	4.103	3.061	1	
10	28.78	42.20	0.447	1.388	36.44	22.18	92.15	4.098	3.062	1	

PICTURE MANIPULATION

Two of the functions that are used inside the measurement procedures are also available separately, mostly for export, evaluation and error-checking purposes.

To take a picture

You take e picture by selecting Measure | Take a picture. A picture is "taken" by capturing a picture from the video camera and presenting it on the screen. It will then also be present in the internal picture buffer and may be filtered or saved.

The speed button  has the same function.

Filter picture

A picture that is present on screen may be filtered by selecting Measure | Filter picture. The function "filters" a picture by determining the profile's xy-co-ordinates. When you choose the function, the measure window will show in the same way as during a surface tension or contact angle experiment, the heading will be Set cursor position and the Start button will be named Filter. The crosshair cursor will appear, but because the program has no way of knowing what kind of picture is presented, the crosshair cursor now starts in the middle of the screen. You must then move the cursor to the desired position to mask the unwanted parts of the picture (if any) and start the edge detection in the correct part (as

described above) before clicking Filter or pressing the <Enter> key. The filtered profile will stay in memory and on-screen until a new picture is fetched. The profile-data may be saved to a (binary) data file or to a text file as described in the section on files.

VIEW MENU

The view menu contains controls for the frame grabber and for some of the main windows.

Start/Stop passthru

This function is a toggle that shows or hides the live video image (in the passthru window or the Main window, see below). Passthru may be automatically switched on at program startup by selecting this in the Options dialog (see Options). It may also be switched on and off during a run by this function. When the program grabs a picture, passthru is switched off preliminary.

Passthru in Main/Separate window

As an alternative (from V1.4.05) the Main window may be used also as the passthru window. This function may be activated by selecting View | Passthru in Main window, and deactivated by View | Passthru in Separate window (the text on the menu is context dependent). Passthru must be switched **off** for this menu line to be enabled.

It should be noted that fast measurements may take considerably longer time when the Main window is used for passthru and Plot profile in picture is selected in the Options dialog.

When the Main window is used for passthru, the "live" image is sitched off automatically when the widow is needed for displaying saved images, as for instance when doing recalculations.

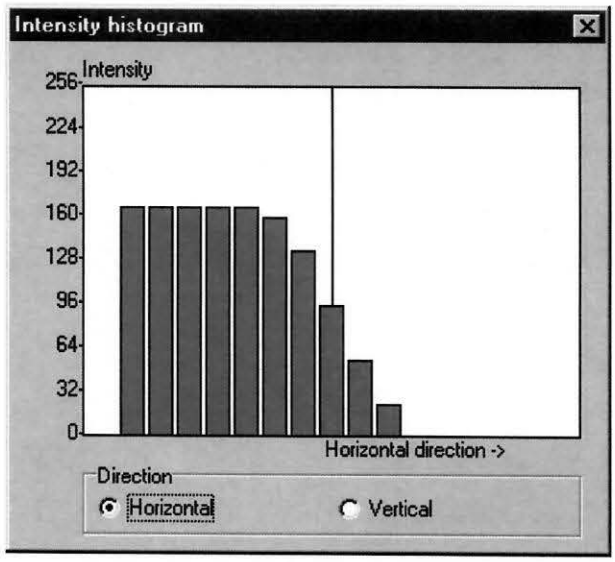
Show/Hide results window

The results window is shown automatically when the program wants to display results, but may also be switched on and off by this function. This function is also a toggle.

Intensity histogram

An intensity histogram is a bargraph of the intensity values (0-255) of a horizontal or vertical row of pixels. This function may be useful in the setup and adjustment of the optical system and in error detection (to check where the intensity change has its maximum). When the function is selected, a picture is «taken» as described above, and the white crosshair cursor is shown in the middle of the picture. This may be moved by means of the mouse and arrow keys as outlined in the measurement section. The histogram contains 15 bars with the co-ordinates of the cursor (crosshair) as midpoint and is updated continuously whenever the cursor is moved. An example of a histogram is shown below.

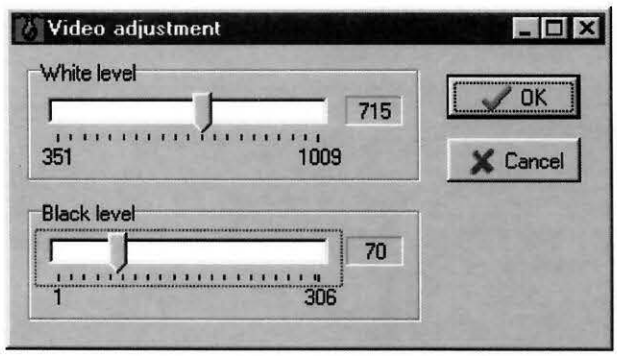
The Intensity histogram



The x-axis of the histogram initially corresponds to the horizontal direction in the picture, but this may be changed to the vertical direction by selecting the Vertical radio button. If a picture is presently visible on the screen, a new picture is not taken, meaning that a picture that is loaded from a file may also be analyzed in this way.

Video adjustment

The Video adjustment control



Video adjustment means setting of the black and white limits for the frame grabber board. The black level is the intensity (in millivolts) below which all image data is considered as black (=0). The white level is the intensity above which all image data is considered as white (=255). This means that the image data is only converted between these two limits, and the intensity scale is linear in this region.

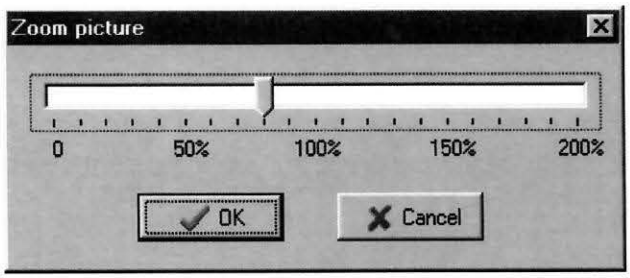
The two sliders may be moved by the mouse, or first clicked (or tabbed to) and then moved by the left and right arrow keys or the <Page Up> and <Page Down> keys. The passthru image is adjusted immediately, the captured image at next capture.

It may be an advantage to adjust the black and white levels to make the contrast as high as possible. This will usually improve accuracy of the calculated data. However, the contrast should not be too high, as this may remove information from the picture. You should not change the contrast after a calibration has been performed; if this is done, then calibration should be repeated. It should not be necessary, however, to adjust the aspect ratio. Optimal values for black and white level are set in order to give the darkest parts and intensity close to 0 (if possible), and the most intense parts close to 255. The Intensity histogram function may be used to observe these intensities.

Zoom picture

In order to keep the correct aspect ratio the captured image cannot be sized by grabbing its borders or corners, however, the image may be sized by the Zoom picture function. This menu item has a submenu where you can select 200%, 100%, 75%, 50% or Other... The 100% magnification means that one image pixel is one pixel on screen, the other magnifications are relative to this. If you select Other..., the dialog shown below appears.

The Zoom picture control

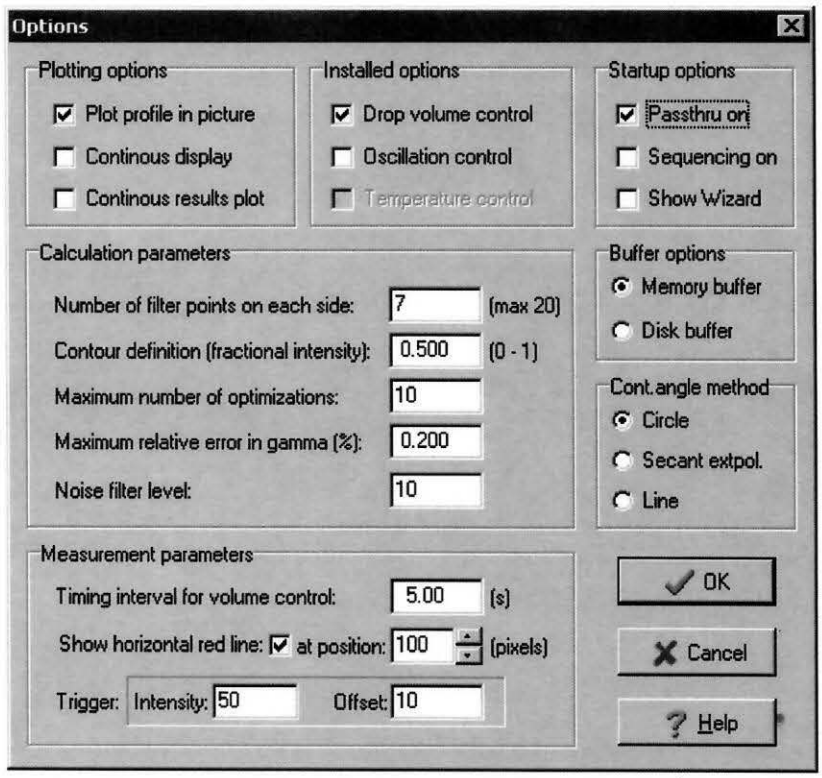


The slider may be used to set a scale between 0 and 200%, in steps of 10%. The scale will be remembered between sessions. If the image is too big for the main window, scroll sliders will appear.

OPTIONS

Many of the default control parameters for DROPimage may be changed from the **Options window** that is shown below.

The Options window



Plotting options

In the Plotting options group the first checkbox is Plot profile in picture. This determines if the profile should be plotted after a filter operation. The Continuos display box determines if the picture is updated after each measurement in an experiment. Continuos result plot determines if the results are graphed (in the graph window) during an experiment. These 3 options are saved in the initialization file (drop.ini).

Installed options

These 3 checkboxes tell the system which of the 3 possible hardware control options that are installed in the system. The checking of one of these boxes enables the corresponding menu function in the Device control menu, in addition

to the different functions connected to these devices. The program does not check if a device really is present, so if you enable one of these options where the device is not present, the program may crash when trying to access the device. Options that are not supported in the present version of DROPimage will be grayed.

Calculation parameters

Some of the parameters used in filtering and calculations may be adjusted here. The parameters are saved between sessions in the dropwin.ini file.

Number of filter points on each side (=n) means the pixel points that are used in the edge detection (filtering). A total number of 2n+1 points are used, meaning that when n=7 the total number is 15. Increasing n to a maximum of 20 may improve the stability of the edge detection algorithm, especially if the edge is not well defined (less sharp), but will lead to longer filter times. On the other hand, the number n may also be decreased in certain cases, especially when measuring very small drops or drops with difficult contrast conditions.

Contour definition (fractional intensity) parameter is the fraction F in the edge definition (in Equation [1], Appendix 1A). It may be set to any value between 0 and 1 but our experience indicates that values between 0.5 and 0.6 are best. The value may possibly influence the degree of dependence of magnification on γ (γ should be independent of magnification).

Maximum number of optimizations is self-explaining. A high number here will possibly improve the chance of obtaining an optimized value in some instances, but experience has showed that if this number exceeds 5-6, the quality of the profile data is bad, meaning the drop is either unsymmetrical, or there is some other (optical) problem.

Maximum relative error in gamma is also used in the optimization procedure. The procedure will continue until the maximum relative error is subsided, or the maximum number is exceeded.

Noise filter level is the maximum "noise" difference between two neighbor pixels that is allowed in the initial determination of the profile starting point. The profile start seeking routine looks along the vertical line of the crosshair cursor. When the difference between two intensity values is greater then Noise filter level, the program determines that point as the start of the profile. It may therefore be necessary to adjust this parameter to fit the lighting and general picture conditions. A too low or too high value may lead to that the profile is not found.

Measurement parameters

Timing interval for volume control is used when the Keep constant option in the Method is volume or area. The interval is the time, in seconds, before the first volume measurement and between volume measurements. As a volume measurement consists of one profile determination and a numerical integration, it is quite fast, and this interval can be set to a few (5-10) seconds.

Show horizontal mask selects if and where a horizontal line is displayed in the main picture. This line acts as a mask in order to avoid disturbing objects in the top or bottom of the picture. If the line is in the **upper half** of the picture, the part of the picture **above** the line will be excluded from all filter operations, if the line is in the **lower half**, the part **below** the line will be excluded. The line may be moved directly by means of the mouse, by holding down the *Ctrl k*ey and the *Left* mouse button. The position in the Options window will be changed accordingly.

Trigger controls the intensity and offset of the trigger function, if used. The trigger is activated when the average intensity of the trigger pixels drops **below** the value in the Intensity box. The value in the Offset box determines the distance, in pixels, between the horizontal cursor line and the trigger pixels. A **positive** distance points against the **middle** of the picture. The trigger pixels are 15 pixels in a horizontal line, 7 at each side of the vertical (left) cursor line.

Startup options

There are three startup options, Passthru on, Sequencing on, and Show Wizard. The first determines if the live video image display is on at program start, while the second determines if the sequencing ability is on at startup. Both these functions may be toggled on and off in the program. The third option in this group selects if the New Experiment Wizard is displayed first when the program is started. This option may also be switched on and of in the first window of the Wizard.

Buffer options

These radio buttons select if DROPimage uses a memory buffer or a disk buffer to save bitmaps during fast measurements. A memory buffer is a preliminary buffer that stores the images at real-time non-interlaced video rates (up to 60 Hz), but has a limited capacity. The capacity is dependent on how much memory the PC has, and on the operating system (Win95/98/ME, or Win NT/2000/XP). Usually ca 150 pictures may be stored if the PC has 128 MB RAM; if more pictures are used, the system may slow down considerably, as virtual memory will be used (the swap file). When using a disk buffer a practically unlimited number of pictures may be grabbed (there is an upper limit of 4 GB in FAT32 systems, ca 10000 pictures in CCIR systems). The disk buffer may be slower than

the memory buffer, however, but the speed is highly dependent on the PC and the operating system. In a system with processor speed at or above 800 MHz and a fast disk (7200 rpm or above), the disk buffer may be as fast as the memory buffer. It should be noted that Data storage in the Method cannot be set to Bitmap (raw) if a memory buffer is used.

Cont.angle method

The **Cont.angle Method** group selects which extrapolation method to use for the contact angle calculations. Please see **Using the Contact Angle tool** for further explanation.

DEVICES AND DEVICE CONTROL

In the **Device control menu** the functions are collected that opens the control windows of the devices that may be present in the system. The possible devices are Volume control, Oscillation control and Temperature control. The devices are selected from the Devices group in the Options dialog that are selected by the Edit | Options function. The control selection function for the selected devices will then be enabled in the Devices menu.

Volume control

The program supports a auto syringe for the control of the drop volume. The auto syringe is used by the measurement procedures, but may also be controlled from the Volume control window as shown below.

The window contains controls for general input and output of liquids and for setting some of the auto syringe's control values.

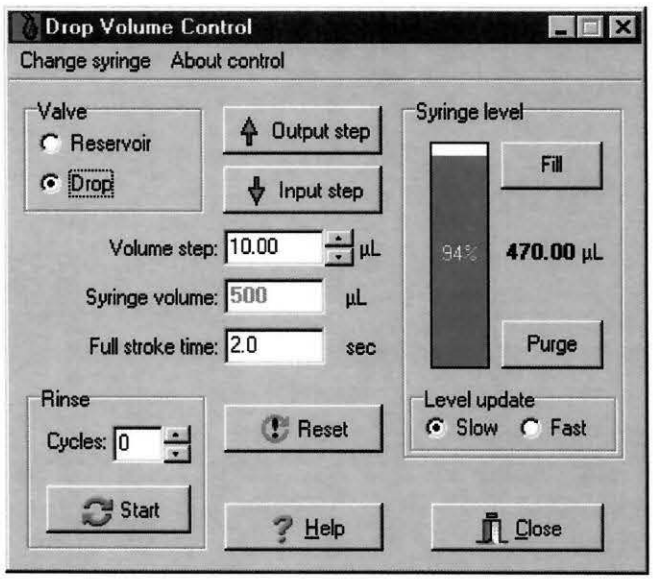
The Valve group manually turns the auto syringe's valve. When the auto syringe is used by a DROPimage method, the valve is controlled automatically.

The Syringe level indicator follows the syringe when controlled from this program. The level is saved between runs in the initialization file (dispens.ini). In order to synchronize the program and the auto syringe the Reset button sets both to the same state (empty). In addition the auto syringe must be reset every time it is turned off and on again. By keeping the auto syringe turned on, DROPimage may be stopped and started without resetting the auto syringe.

The Level update buttons determine if the level indicator will be synchronized to the syringe speed, or updated immediately. *If you use an experiment that controls*

the auto syringe directly, Level update *should be set to* Fast *in order to avoid delays in the measurement.*

The Volume control window



The Syringe volume field cannot be edited but is changed by the Change syringe menu. The program cannot check if the syringe size is the one really installed. If it is wrong, the volume control will not work properly.

The measurement program is not affected by the Volume step setting, it will use the steps required by the Method. If the Keep constant combo box in the Method is volume or area, the volume step will be dependent on the deviation. The minimum step will be used if the deviation is more than 50% of the minimum step.

NOTE: The auto syringe control has its separate initialization file, DISPENS.INI. This file may look as shown below.

[Settings]	
Level=0	Saves the syringe level between runs.
Volume=250	The syringe volume
Speed=5	The syringe speed
StepVolume=1.0	The volume step
[Com]	These parameters determine the communication
Port=1	port settings. They can be changed by editing
Enabled=1	the DISPENS.INI file with a text editor
BaudRate=9600	(for instance Notepad).
ByteSize=8	
Parity=0	

StopBits=2

[Screen]
VolumeTop=27
VolumeLeft=559

These parameters save the auto syringe control's screen position between runs.

SURFACE ENERGY TOOLS

DROPimage contains a selection of tools for the calculation of surface energies of solids from measured contact angles. The tools work on Contact Angle (CA) Files that are made and edited in the Contact Angle File Control (CAFC). The format of the contact angle files is the same as in the RHI2001 contact angle tools and the tools in DROPimage also closely correspond to the RHI2001 tools.

The main difference between the tools on DROPimage and RHI2001 is that in some of the tools of DROPimage standard deviations are calculated. In addition, the Solid-Liquid-Liquid Surface Energy tool is unique to DROPimage. The latter tool makes it possible to measure the surface energies of high-energy solids like metals and metal oxides by using the contact angle of one liquid (usually water) when the solid is covered by (submerged in) another liquid (usually a hydrocarbon).

In DROPimage timed contact angles are measured either as the byproduct of interfacial tension measurements, preferably of sessile drops or bubbles, or by a timed contact angle method. Results from these methods are saved in log-files (of type *.LOG) and the CAFC will read these log-files and produce CA Files. The CAFC is very flexible and makes it possible to incorporate CA measurements from different runs in one CA file. The CAFC is described further in the section "Working with DROPimage files".

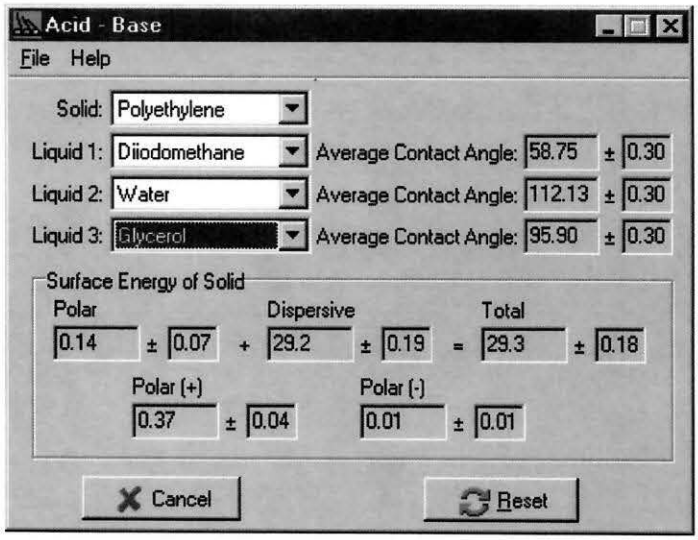
The surface energy tools are available through the Tools menu and contain the following separate tools:

- Acid – Base tool (3 liquids)
- Surface Energy tool (2 liquids)
- Work of Adhesion tool (1 liquid)
- Zisman's Plot tool
- Solid-Liquid-Liquid Surface Energy tool

There is a common structure to all tools: The File | Open menu command opens a Contact Angle file. The records of this file are active ("live") records, which means that the data in the file are available to all tools without being reopened. It also means that the data are available in the CAFC at the same time (the right

pane). This also means that data in the right pane of the CAFC are at the same time open in all the tools.

Acid - Base Tool



Purpose

The 'Acid-Base Tool' evaluates the surface energy parameters of a given solid using the contact angles of three different test liquids. Van Oss et al have shown that the contribution due to acid-base interactions can be expressed in terms of the product of their electron donor and electron acceptor components by using three liquids, one apolar and two polar. Recommended test liquids are methylene iodide or bromonaphthalene for the apolar liquid and a polar liquid pair of either water and glycerol or water and formamide.

Reference:

1. C.J. van Oss, R.J. Good and M.K. Chaudhury; Adv. Colloid Interface Sci. 28, 35 (1987).
2. C.J. van Oss, R.J. Good and M.K. Chaudhury, J.; Chromatography 191, 53 (1987).
3. C.J. van Oss, R.J. Good and M.K. Chaudhury, J.; Langmuir 4, 884 (1988).

Procedure

This is a step by step procedure of how to use the Acid-Base Tool:

Step 1. Open the Acid-Base Tool.

Step 2. Select File | Open from the Acid-Base Tool's menu and open one or more files generated by the Contact Angle File Control or by the Contact Angle Tool in RH Imaging 2001 (denoted by the *.ca extension). In this example the Parafilm.ca

file is used. If one or more files are already opened in the Contact Angle File Control, the new records are added to those already present. All active data are shown in the Contact Angle File Control.

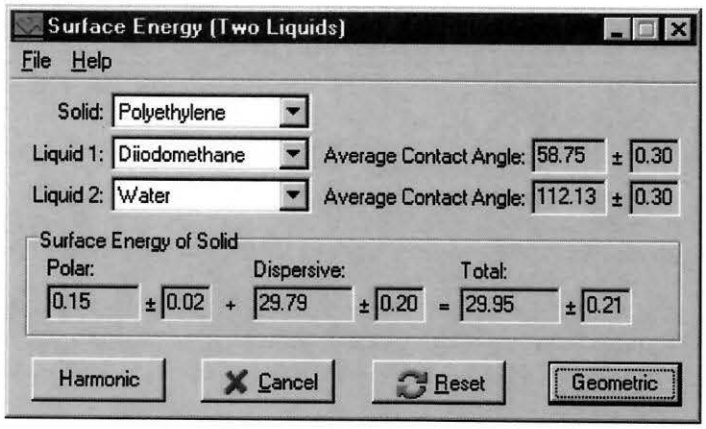
Step 3. Select the desired Solid, Liquid 1, Liquid 2, and Liquid 3 from the drop down lists.

Step 4. The surface energy measurements are automatically calculated when the appropriate solid and liquid combinations are selected. The results are displayed in the Surface Energy of Solid section.

The Close button closes the window, but keeps the live data.

The Reset button erases all live data, but does not close the window.

Surface Energy (Two Liquids) Tool



Purpose

The 'Surface Energy Tool' evaluates the surface energy of a given solid using the contact angles of different test liquids.

The geometric-mean method uses two pure liquids denoting their dispersive and non-dispersive values. Water and methylene iodide are a convenient choice for test liquids. Different liquid pairs tend to give different results. The surface energies and polarities of some low-energy solids obtained by this method are often much lower than those calculated by other methods.

Reference: D.K. Owens and R.C. Wendt, J Appl Polym. Sci. 13, 1741 (1969).

The harmonic-mean method also uses two liquids in its calculations. The results obtained with this method are regarded as accurate by Wu and agree remarkably well with other methods. Wu claims that this method is especially suitable for polymers, but this finding has, however been disputed. Some researchers consider that non-dispersive interactions across interfaces are mainly of acid-base nature and in that situation recommend using the acid/base tool. The harmonic-mean method may not always give a solution, depending on the measured data.

Reference: S. Wu, J Polym. Sci C34, 19 (1971).

Procedure

This is a step by step example of how to use the Surface Energy Tool:

Step 1. Open the Surface Energy Tool.

Step 2. Select File|Open from the Surface Energy Tool's menu and open one or more files generated by the Contact Angle File Control or by the Contact Angle Tool in RH Imaging 2001 (denoted by the *.ca extension). In this example the Parafilm.ca file is used. If one or more files are already opened in the Contact Angle File Control, the new records are added to those already present. All active data are shown in the Contact Angle File Control.

Step 3. Select the desired Solid, Liquid 1and Liquid 2 from the drop down lists.

Step 4. To calculate the surface energy using the harmonic method, click on the Harmonic button.

To calculate the surface energy using the geometric method, click on the Geometric button. The results will be displayed in the Surface Energy of Solid area.

The Close button closes the window, but keeps the live data.

The Reset button erases all live data, but does not close the window.

Work of Adhesion Tool

Purpose

The 'Work of Adhesion Tool' determines an index of wetting ability of a liquid for a solid. The Adsorption Theory proposes that van der Waals interactions should be sufficient for good adhesion. The liquid/solid thermodynamic considerations give rise to this equation relating the reversible work of adhesion and surface free energies according to Young and Dupre, noting that the process of adhesion may be described in terms of opposites, namely the process of separation.

Reference:
Buff, F.P. "The theory of capillarity", in Encyclopedia of Physics; Flugge, S., Ed: Springer-Verlag: Berlin, 1960; pp. 281-304.

Procedure

This is a step by step example of how to use the Work of Adhesion Tool:

Step 1. Open the Work of Adhesion Tool.

Step 2. Select File|Open from the Work of Adhesion Tool's menu and open one or more files generated by the Contact Angle File Control or by the Contact Angle Tool in RH Imaging 2001 (denoted by the *.ca extension). In this example the Parafilm.ca file is used. If one or more files are already opened in the Contact Angle File Control, the new records are added to those already present. All active data are shown in the Contact Angle File Control.

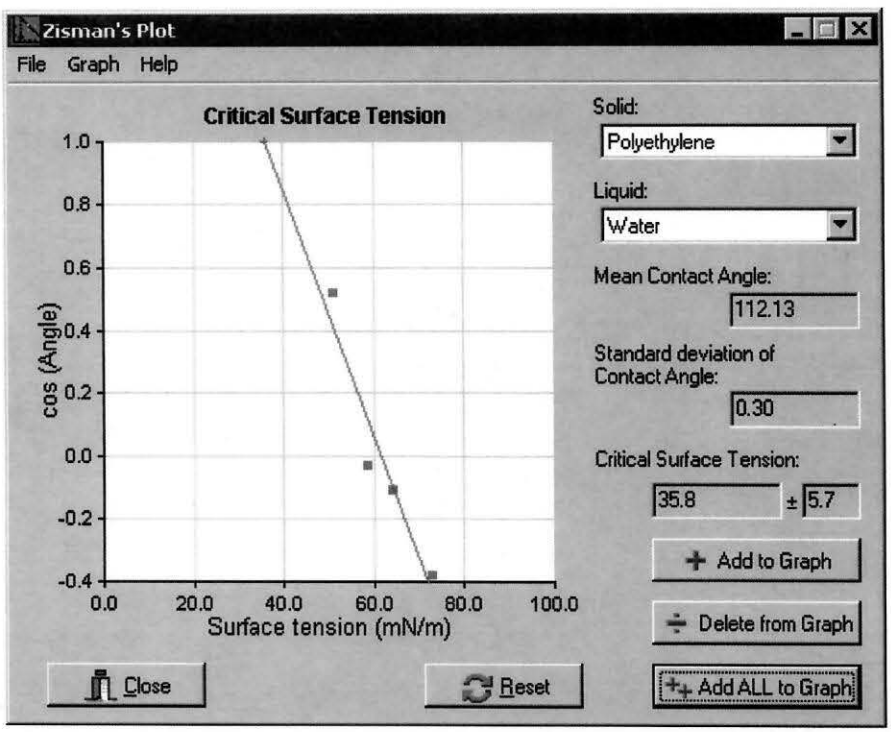
Step 3. Select the desired Solid and Liquid from the drop down lists.

Step 4. The work of adhesion measurement is automatically calculated when the appropriate solid and liquid combination is selected.

The Close button closes the window, but keeps the live data.

The Reset button erases all live data, but does not close the window.

Zisman's Plot Tool



Purpose

The 'Zisman's Plot Tool' summarizes wetting behavior and allows predictions of an interpolative nature using a homologous series of liquids. Extensive series of measurements of contact angles of various liquids on low-energy polymer substrates were reported by W.A. Zisman, inventor of the Ramé-Hart Contact Angle Goniometer, and his coworkers at the Naval Research Laboratory. An empirical linear relation was found between the cosine of the contact angle and the surface tension of the liquid of the sessile drop. The extrapolation of the line to $\cos(\theta) = 1$ gives the "critical surface tension" of the substrate.

The term "critical" is used because any liquid on the Zisman plot whose surface tension is greater than the "critical surface tension" makes a finite contact angle with the substrate. Critical surface tension values are useful empirical values that

characterize relative degrees of surface energy of polymer substrates. Zisman's empirical prediction fails for liquids that form hydrogen bonds or acid-base interactions with the substrate. These liquids would spread spontaneously on the substrate.

Reference: W.A. Zisman, ACS Adv. Chem. Ser. 43, 1 (1964).

Procedure

This is a step by step example of how to use the Zisman's Plot Tool:

Step 1. Open the Zisman's Plot Tool.

Step 2. Select File|Open from the Zisman's Plot Tool's menu and open one or more files generated by the Contact Angle File Control or by the Contact Angle Tool in RH Imaging 2001 (denoted by the *.ca extension). In this example the Parafilm.ca file is used. If one or more files are already opened in the Contact Angle File Control, the new records are added to those already present. All active data are shown in the Contact Angle File Control.

Step 3. Select the desired Solid and Liquid from the drop down lists. Click on the Add to Graph button. Select a second Liquid and click on the Add to Graph button. Two or more solid/liquid combinations must be chosen in order for points to be plotted on the graph.

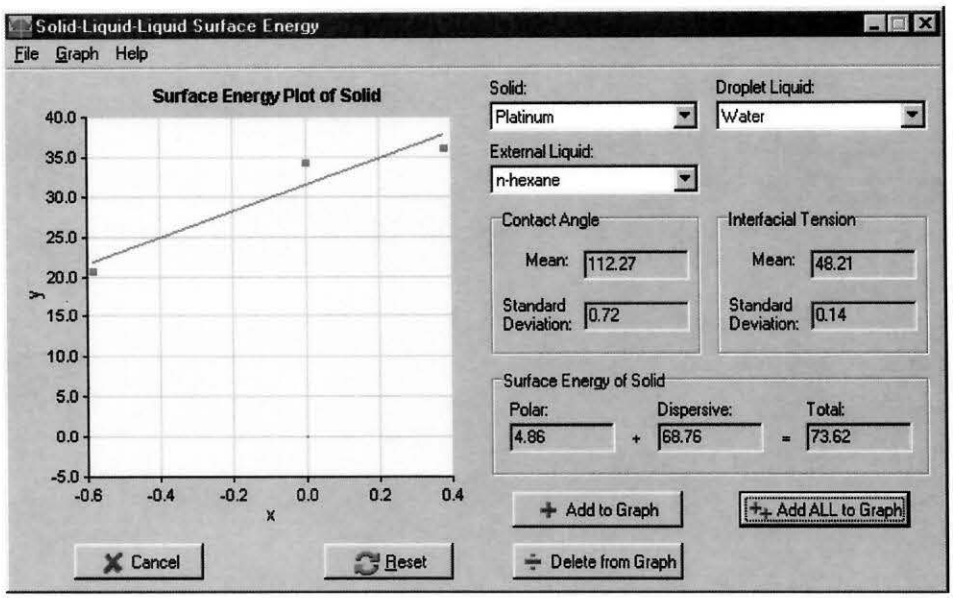
Note: Click on the Add ALL to Graph button to automatically plot each point on the graph.

Step 5. The critical surface tension for the given solid is automatically calculated when two or more solid/liquid combinations have been selected. The error given is calculated from the Standard Error of the regression in the x-direction at the critical surface tension.

The Close button closes the window, but keeps the live data.

The Reset button erases the plot and all live data, but does not close the window.

Solid-Liquid-Liquid Surface Energy Tool



Purpose

The 'Solid-Liquid-Liquid Surface Energy Tool' evaluates the surface energy of a given solid using the contact angles of one test liquid on a solid submerged in a series of different liquids according to the method of Shultz et al. According to this method a plot of $\gamma_W - \gamma_H + \gamma_{WH}\cos\theta$ vs. $(\gamma_W^d)^{1/2} - (\gamma_H)^{1/2}$ gives a straight line with the intersection $E_{SW} = 2(\gamma_S^p\gamma_W^p)^{1/2}$ and slope $2(\gamma_S^d)^{1/2}$. From these values the surface energy of the solid, γ_S^d (dispersive) and γ_S^p (polar) are calculated. (Here W denotes the polar liquid, usually water, and H the external unpolar liquid, usually a hydrocarbon). It is noted that the interfacial tension γ_{WH} is needed for this calculation. Mutual solubility between the two liquids may be a problem with this method.

Water or formamide is usually used as the test liquid and a series of hydrocarbons as the continuos phase (hexane, cycohexane, octane, decane, hexadecane). At least 2 different liquids must be used. The method is especially useful for high-energy solids as metals and oxides that are otherwise wetted by most liquids.

Reference:
J.Schultz, K.Tsutsumi and J.-B. Donnet, J.Colloid Interface Sci 59, 272 and 277 (1977)

Procedure

This is a step by step example of how to use the Solid-Liquid-Liquid Surface Energy Tool:

Step 1. Open the Solid-Liquid-Liquid (SLL) Surface Energy Tool.

Step 2. Select File|Open from the SLL Surface Energy Tool's menu and open one or more files generated by the Contact Angle File Control or by the Contact Angle Tool in RH Imaging 2001 (denoted by the *.ca extension). In this example the Platinum.ca file is used. If one or more files are already opened in the Contact Angle File Control, the new records are added to those already present. All active data are shown in the Contact Angle File Control. The Contact Angle File may contain surface tension data in addition to contact angles.

Step 3. Select the desired Solid and Droplet Liquid from the drop down lists. Select one External Liquid and click on the Add to Graph button. Select a second External Liquid and click on the Add to Graph button. Two or more external liquids must be chosen in order for points to be plotted on the graph. The interfacial tension between the Droplet liquid and External liquids may be included in the Contact Angle file if the file is produced from normal interfacial tension results (both contact angle and interfacial tension are calculated). If the interfacial tension is not present in the file, the Interfacial Tension box will become white, and you must input the interfacial tension in the box.

Note: Click on the Add ALL to Graph button to automatically add all External Liquids to the graph. This can only be used if ALL interfacial tensions are present in the file(s).

Step 5. The surface energy for the given solid is automatically calculated when two or more liquid-liquid combinations have been selected.

The Close button closes the window, but keeps the live data.

The Reset button erases the plot and all live data, but does not close the window.

FILE DESCRIPTION

DROPimage comes with a number of files that are installed in the program directory on the hard disk (usually c:\DropImage\Data). Some of these files may be changed by the user either in the program or (in the case of text files) by an external text editor. The files are described below.

DROPIMG.EXE The DROPimage Advanced program file (binary).

DISPENSX.DLL
The driver for the external auto syringe. This file is hardware dependent, and must be exchanged by a new file by the same name if another auto syringe is installed.

DROP.CAL Calibration file (Text). This file consists of 3 numbers, each on a separate line. They are the lengths, in mm, of a pixel in the x-direction (vertical) the y-direction (horizontal), and the aspect ratio (= y/x). This file is rewritten every time a new calibration or aspect ratio adjustment is performed.

DEFAULT.BMP Startup picture (bitmap). This bitmap will only show if the program cannot take a picture when it is supposed to do so. The image helps to optimize the Windows color palette for the captured images.

DEFAULT.MET Default method (text). This and all other method files consist of the records in the Method Editor, each on a separate line. They should, however, only be changed by the Method Editor (the upper/lower case in the keywords is significant).

DEFAULT.PAR Default parameters (text). This and all other parameter files consist of the records used in the Parameter Editor, each on a separate line. In addition, the pixel dimensions x and y are saved in the 2 last lines for use in case of recalculation. **If you run a new experiment with the same name as an old experiment but with a different magnification, recalculation of stored data from the old experiment will be wrong!**

DEFAULT.TIM Default time file.

DEFAULT.SES Default session file (text). The session file contains a list of experiments (LOG-file names) in an experimental session. Each experiment is on a separate line.

LIQUIDS.TXT Lists a number of liquids including surface tension data and density

SOLIDS.TXT Lists a number of solids including surface tension data and density

SYRINGES.TXT Lists the possible syringe volumes that may be used by the auto syringe.

DROP.INI Configuration file (text). This file contains the setup parameters which are read by the program at start-up, and which determine many of the program's properties. The file is stored in the DropImage directory together with the other files. An example of this file is shown below.

The file names in the **[Files]** group are the default file names used.

The parameters in the **[Installed]** group define the external units installed in the system. The Horizontal and Vertical constants define the startup size for the frame grabber bitmap. The ToolsMenu parameter switches the Tools menu on and off.

In the **[Calculation]** group are parameters from the Options window. They are defined above under Options. The Baseline parameter is the start position of the horizontal crosshair cursor in a sessile drop or timed contact angle experiment, measured in pixels from the top of the picture. The parameters *MaxSkewness* and *MaxSideDiff* serve to protect against "strange" drop pictures. If the drop profile is not properly detected, for instance due to optical conditions, the program may hang if it tries to do calculations on such "strange" data. The program must then be restarted, and sometimes the whole computer may have to be restarted because of problems with the initialization of frame grabber's driver. These parameters may only be changed by editing the DROP.INI file with a text editor (such as Notepad). "Good" drops in equilibrium will very rarely give problems. If you have problems with drops close to the "good" limit, you may want to experiment with these parameters. You may want to decrease both parameters to force the program only to calculate "perfect" drops. The OscillPoints and OscillPeriod parameters save the settings of the oscillation fields in the Method editor.

The numbers in the **[Calibrate]** group are the default size, in mm, for the cylinder (rod) and sphere used for calibration; the

SyringeVolume parameter is the volume, in µL, of the syringe used in the volume control auto syringe.

In the **[Screen]** group are the positions of some of the more important windows that are saved between sessions. The first 4 items refers to the main program, Res refers to the results window and Video to the live (passthru) window. The number of items in this section may vary between different versions of DROPimage.

The **[Settings]** parameters save the black and white levels for the frame grabber and the rest are the Startup options. In this section is also saved some of the parameters in the Options window. The parameters are mostly self-explanatory.

```
[Files]
Method=DEFAULT.MET
Parameters=DEFAULT.PAR
TimeFile=DEFAULT.TIM
DropDirectory=C:\DropImage\Data

[Installed]
VolumeControl=1
OscillationControl=0
TemperatureControl=0
ToolsMenu=1
Horizontal=640
Vertical=480

[Calculation]
Baseline=265
FilterPoints=7
Threshold=0.550
Optimize=10
MaxError=0.00200
GrabLimit=0.500
VolumeTiming=5.00
NoiseLimit=10
OscillPoints=40
OscillPerionds=4
MaxSkewness=0.100
MaxSideDiff=0.100
TriggerThreshold=50
TriggerOffset=10

[Calibrate]
Cylinder=4.000
Sphere=4.000
SyringeVolume=250

[Screen]
Top=30
```

```
Left=65
Height=498
Width=502
ResTop=69
ResLeft=216
ResHeight=552
ResWidth=670
VideoTop=169
VideoLeft=574
Zoom=0.75
ParameterTop=52
ParameterLeft=591
StartFormTop=510
StartFormLeft=604
ChartTop=391
ChartLeft=550
StatusTop=20
StatusLeft=40

[Settings]
BlackLevel=87000
WhiteLevel=644000
PassthruOn=0
SequencingOn=0
FrameType=1
ContinousDisplay=0
PlotInPicture=1
ContinousGraph=0
WizardOn=0
```

DISPENS.INI Configuration file (text) for the auto syringe. This file contains the setup parameters which are read by the program at start-up, and which determine many of the auto syringe's properties. The file is stored in the DropImage directory together with the other files, or in the Dispens directory in case you have installed the separate auto syringe control program. An example of this file is shown below.

```
[Settings]
Level=3000
Volume=250
Speed=2
StepVolume=1.00

[Com]
Port=1
Enabled=1
BaudRate=9600
ByteSize=8
Parity=0
StopBits=1

[Screen]
VolumeTop=121
```

VolumeLeft=523

The [Settings] section saves the current auto syringe level (in steps), Speed and Step volume settings between runs, and the syringe volume. The [Com] section sets the parameters for RS232C serial communication port on the PC. These parameters must correspond to those of the auto syringe. You should usually only need to change the port number (Port=1 is Com1 and Port=2 is Com2, etc.) and to set Enabled=0 if you wish to run DROPimage without a auto syringe. The [Screen] section saves the position of the Volume control window between runs.

Different data files written by the program

The name of these files is the same as the experiment name, i.e. the parameter file name without the extension. The program then adds the file type. For data files in a series, i.e. PIC and DAT files, the picture number is in the file name, enclosed in brackets and starting at 0 (example: Test[9].DAT is profile number 10 in the Test experiment).

.DAT (Binary) Filtered drop profile data.

.LOG (Text) Log-files. All time-controlled results are written to a log-file. The first line in the file is the heading line, corresponding to the results window's header.

.PIC (Binary) Picture pixel data. The size is dependent of the frame grabber board and video standard. The bytes are ordered consecutively and by line starting with the upper left byte (0,0). The files contain only uncompressed bitmap data and no file headers.

.BMP (Binary) Bitmap pixel data. The format is the standard Windows-OS/2 bitmap format. The palette is 8 bits, 256 grays. The file is uncompressed.

.TIF (Binary) Bitmap pixel data. Tagged Image File Format. The format used here is similar to the BMP-format and is uncompressed.

.GIF (Binary) Bitmap pixel data. Graphic Interchange Format (CompuServe). This format is the one most often used on the Internet. It is also an 8-bit format, 256 grays, but is compressed (loss-free) and may be used to store images in order to take less space.

.RTF (Rich text) Report files. The text in the report window as formatted for the printer and written to a rich text file. RTF files may be read (and written) by most word processing programs, in addition to other programs.

.RTI (Text) Real Time files: Actual time values for experiments that store data either in pixel or profile-data files.

.TXT (Text) Filtered drop profile data saved in text format instead of binary .DAT-format. One x and y-value per line, with spaces between. The files are for export only.

.SES (Text) Session file that consist of a list of log files.

.OSC (Text) Oscillation file that consists of a list of the log files that contains a series of frequencies in an oscillation experiment.

.CA (Binary) Contact angle file that contains results form contact angle measurements and that are used in the Rame-Hart and DROPimage surface energy Tools. The format is copyright Rame-Hart.

APPENDIX 1

DESCRIPTION OF THE PHYSICAL AND MATHEMATICAL METHODS

Edge tracing

The video image consists of an array of pixels (dependent on the frame grabber board), each with 256 levels of light intensity (gray levels). The filter routine for detection of the drop profile is a simple edge-tracing routine with increased (sub-pixel) accuracy compared to global tresholding and maximum gradient techniques. In order to discriminate the drop interface the program uses a local threshold and interpolation routine. The co-ordinates of the drop profile are found by linear interpolation to a given fraction, F, between the local maximum and minimum of light intensity, i.e.

$$I_{threshold} = F \times (I_{max} - I_{min}) \qquad [1]$$

From analysis of gray levels in the neighborhood of the drop interface, the value 0.55 is used as a suitable value for this fraction. However, as the value has considerable influence on the final result (see below) a comparison of this method against liquids of known surface tension will indicate the optimal value. One of the co-ordinates for each point is an integer (0-255) and the other will be a decimal number because of the interpolation routine. The accuracy is thus considerably improved compared to simple global tresholding or maximum gradient routines that gives both co-ordinates as integers.

Once a point on the drop profile has been found, the search for the next point is limited to the nearest point on the next line. In the bottom part of the drop the search direction is switched from horizontal to vertical. Most drop profiles consist of from 700 to 1000 points. On the average the routine uses from 2 to 3 seconds on these calculations. The same filter routine is used for discriminating the drop interface when using the program for contact angle measurements.

Determination of initial size parameters

Theoretical background

A 2-step process determines surface tension. First, size parameters R_0 and β are determined from the drop profile, secondly surface tension is calculated from these parameters by the equation,

$$\gamma = \Delta\rho \, g \, R_0^2 / \beta \qquad [2]$$

Here $\Delta\rho$ is the mass density difference between the drop and the surrounding medium, g is the gravity constant, R_0 is the radius of curvature at the drop apex and β is the shape factor, as defined by this equation. By convention, $\Delta\rho$ is defined such that $\Delta\rho$ and β is negative for pendant drops, and positive for sessile drops.

The equations describing the drop profile are derived from the Young-Laplace equation and may be represented in dimensionless form:

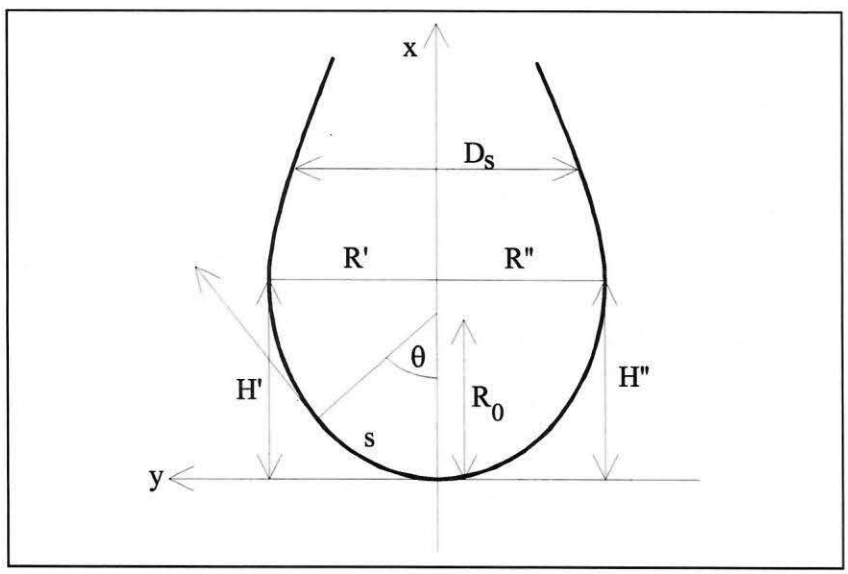
$$d\theta/dS = 2 - \beta Y - \sin\theta / X \qquad [3]$$

$$dX/dS = \cos\theta \qquad [4]$$

$$dY/dS = \sin\theta \qquad [5]$$

The co-ordinates x, y, s and θ are illustrated below.

Dimensions and symbols used in this program



The parameter, s, is the distance along the drop profile from the drop apex. X, Y and S are dimensionless parameters made by dividing x, y, and s, respectively, by R_0. For pendant drops, β and the density difference, $\Delta\rho$, will be negative, while for sessile drops, β and $\Delta\rho$ are positive. A large number of theoretical dimensionless profiles were calculated for the whole possible β-range, from β= -0.55 to 10^{20} by means of Kutta-Merson's numerical integration algorithm with automatic step length adjustment. The maximum relative error was set to 10^{-4}. Each profile was measured mathematically by using cubic interpolation. In this way, curves correlating the parameters β and R_0 with measurable parameters as indicated in the figure were produced, and these curves were fitted with linear polynomials by the method of least squares.

For "normal" pendant drops (i.e. drops that are sufficiently long in order to measure D_S) the maximum diameter, D_E, and the ratio $\sigma = D_S/D_E$ is used (D_S is the diameter at the distance D_E from the drop apex). The equation found is (β is negative here):

$$\beta = -0.12836 + 0.7577\,\sigma - 1.7713\,\sigma^2 + 0.5426\,\sigma^3 \qquad [6]$$

From the same data, an equation for $D_E/2R_0$ is found:

$$D_E/2R_0 = 0.9987 - 0.1971\,\beta - 0.0734\,\beta^2 - 0.34708\,\beta^3 \qquad [7]$$

For pendant drops too short for the determination of D_S, and for all sessile drops, we use the drop "height", H, and the "radius", $R=D_E/2$. If we substitute H for R_0 in Equation [2], we may write,

$$\gamma = \Delta\rho g H^2/B \qquad [8]$$

where B is a transformed shape parameter. For a sessile drop, both R_0 and β may increase several orders of magnitude as the drop becomes large and flat, but in such a way that γ stays the same. It is easily observed that H will have an upper limit because of the maximum hydrostatic pressure the surface tension may "resist". When the drop becomes infinitely wide, only one radius of curvature will be important, and the limiting value of B is 2.0. Equation [8] is therefore much more convenient for sessile drops and may also be used for "short" pendant drops. The parameter B may derived from Equs. [2] and [8] as a function of the ratio ξ=H/R.

$$B = \beta \times (H/R_0)^2 = f(\xi) \qquad [9]$$

Also the dimensionless ratio H/R_0 will be a function of ξ, and we may write

$$H/R_0 = g(\xi) \quad \text{or} \quad R_0 = H/g(\xi) \qquad [10]$$

Combining [8] and [9]: $\beta = f(\xi)/g(\xi)^2$ [11]

The function $B = f(\xi)$ has a maximum B=2.290 at $\xi = 0.285$ that corresponds to ca. $\beta = 5000$. This means that the drop "height", H, also must have a maximum at this value of ξ. This must represent an optimum for the sum of the two radii of curvature, meaning that at higher drop volumes, the curvature in the horizontal plane must decrease stronger than the opposing increase in the vertical plane. The function $B=f(\xi)$ may be mathematically approximated by different functions, depending on the ξ-domain and the desired accuracy. Exact analytical solutions have not been found, but experiments show that ordinary linear polynomials give satisfactory fit in most cases, using ξ-1 as the independent variable and forcing the constant term to 0. Around $\xi=1$ it may approximated by a straight line with a slope of 4.38, while for all values $\xi>0.34$ (i.e. $\beta<1000$) we may use a 4th order polynomial with a standard error of 0.0018. Because of the opposite curvatures of the positive and negative parts of the curve, better accuracy is obtained by using separate equations. Thus for

$\xi<1$: $f(\xi) = -4.1788\,(\xi-1) + 1.9086\,(\xi-1)^2 + 4.5738\,(\xi-1)^3$ [12a]

$\xi>1$: $f(\xi) = -4.3626\,(\xi-1) + 1.1961\,(\xi-1)^2$ [12b]

These equations give very good estimates of B over all regions of practical interest and the slope at $\xi=1$ is 1.723. In order to obtain good estimates for the whole region of $\xi>0.34$, we also choose two separate polynomials that give a standard error of 0.0007.

$\xi<1$: $g(\xi) = 1 + 1.6795\,(\xi-1) - 0.58334\,(\xi-1)^2 - 1.4257\,(\xi-1)^3$ [13a]

$\xi>1$: $g(\xi) = 1 + 1.7356\,(\xi-1) - 0.40869\,(\xi-1)^2$ [13b]

With these two functions, we can easily calculate R_0 and β for all values of $\beta<1000$ from the measurement of H and R and equations [10] and [11].

Experimental procedures

Values for R_0 and β are found from the experimental profile data by several numerical smoothing techniques. For pendant drops, the central axis of the drop is determined by a first order regression line through all data points, using the y-values as the independent and x-values as the dependent variable. For sessile drops, the least square line through the mean values of all corresponding points from the base up to the turning point (45^o) is used. The bottom point of the drop, i.e. the point where the central axis intersects the drop profile, is found by fitting a 4th order polynomial without the 1st and 3dr order terms to all data points in the bottom profile up to a limit of y/x=0.4. The horizontal distance from this mid-line then determines the y-co-ordinates. However, when using sub-pixel resolution,

results may be improved by correcting for small deviations in the vertical direction, i.e. drop skewness. New x-co-ordinates are calculated by the equation

$$x_i' = x_i - \mathbf{a}\, y_i' \qquad x_i'' = x_i - \mathbf{a}\, y_i'' \qquad [14]$$

Here x' and x" are the corrected co-ordinates for the left and right side of the drop, respectively (y' and y" have opposite signs). Indeed, also the y-values may be corrected in a similar way by using the factor $\sqrt{1-a^2}$, but these corrections will be very small because **a** is very small, and may be neglected.

The parameters R and H are determined for each side separately by means of a second order polynomial through 10% of the side's points closest to the maximum. This polynomial has been found to give the most stable determination for most conditions, even if a third order equation principally is more correct because of the unsymmetrical nature of the side profile. For the determination of R_0 and β, the values for the two sides are averaged; in addition an asymmetry factor can be calculated from the equation,

$$Ass = 2\,(H' - H'')/(H' + H'') \qquad [15]$$

The value of Ass gives an indication of the reliability of the final results, as drops with a high asymmetry factor usually give inaccurate results. This method for determination of R_0 and β is used for all sessile drops and for pendant drops where D_S cannot be determined ("short" drops). For ordinary, "long", pendant drops, the method using the ratio D_S/D_E as outlined above is used, because of better accuracy. The value of D_E is simply D_E=R'+R", while the value of the diameter D_S at the distance D_E from the apex is determined by a second order polynomial method similar to that for R' and R".

Fitting of profile data

To achieve even better accuracy and reproducibility of surface tension data, it is necessary to utilize all the profile data in a least squares parameter optimization. The data from the two sides are joined in one profile with origin at the drop apex and direction of the axis as indicated in the figure. In this process, the y-values are corrected for differences between R' and R" by adding and subtracting (R'-R")/2, respectively. This correction results in smaller deviations between data from the two sides, and generally gives better optimization results when the two sides are joined.

Because the initial values of β and R_0 are already quite close to the optimal values, a relatively simple, but yet effective method of second order interpolation/extrapolation (response surface) is used in the optimization. The 9 theoretical profiles in a 3x3 grid around the start values of R_0 and β are calculated

by numerical integration of the Young-Laplace equation, again using Kutta-Merson's algorithm with a maximum relative error of 10^{-4}. The grid granularity is 1% in β and 0.2% in R_0.

The objective function used in the optimization is the normal (i.e. perpendicular) mean square deviation between theoretical and experimental points, given by the equation

$$\Delta f = \frac{\Delta y}{\sqrt{1 + \left(d\hat{y}/dx\right)^2}} \qquad [16]$$

Where the mean square in the y-direction, Δy, is given by,

$$\Delta y^2 = \frac{\sum \left(y - \hat{y}\right)^2}{N} \qquad [17]$$

The mean square is calculated between $x = 0.2\ R_0$ and the maximum value in the data set. N is the number of data points. The theoretical value is calculated at each experimental x-value by means of cubic interpolation (through the 4 closest theoretical data points, 2 on each side).

The result from one profile optimization run is denoted the "contour" method in this program. Sometimes, when working with sessile drops, it may be necessary to repeat the optimization step on order to minimize the error function. The program may be instructed to repeat optimization until a convergence is obtained. This procedure is then denoted "optimized contour". Experiments often show that very little improvement in the value of γ is achieved, especially in the case of large pendant drops. Sessile drops have a much larger span in possible β-values, and are more difficult to optimize, especially at low β-values ($0<\beta<1$), which should be avoided. In addition, sessile drops are more prone to experimental errors that are due to uneven wetting conditions around the drop perimeter, leading to lack of axisymmetry. This phenomenon often results in high asymmetry ratios (several %), and problems with convergence in the optimization procedure, as mentioned above.

Measurement of contact angles.

Theoretical profile

In this program several different methods are used to measure contact angles. The thjeoretical profile method utilizes the theoretical drop profile that is calculated in the curve fitting part of an interfacial tension calculation. This means that the whole drop must be visible, and that the surface must be undisturbed i.e. objects like rods or tubes (pipette) must not be present. Because all the conditions for an interfacial tension measurement must be fulfilled, this contact angle calculation will always be performed when interfacial tensions are measured. Of the theoretical co-ordinates calculated by the numerical integration of the Young-Laplace equation, very few would coincide exactly with the drop's endpoint (the horizontal crosshair cursor). The program will therefore interpolate between the 2 points on each side of the end, using the 2 additional points further away in a cubic interpolation procedure. This interpolation has been shown to give very accurate values compared to the exact theoretical calculation.

Curve fitting

The other methods for calculation of contact angles are pure numeric. The methods are constructed to show a horizontal line on the screen, along which the solid surface is aligned. The filter routine then will give a properly aligned drop profile. The contact angle is easily calculated by numerical derivation of the profile at the contact point. Because of reflection in the substrate and some diffraction, the 2-3 data-points closest to the contact point must be neglected. Different methods of numerical derivation may give considerably different results because of the extrapolation involved. In this program 3 different methods may be selected.

The first (default) uses a least squares curve fit to a circular profile. If only the 50 – 100 data points close to the baseline are used, the profile will be very close to circular. This becomes even more correct for low contact angles, and is considered the best general method.

The second method is a traveling secant method, with linear extrapolation to the contact point is used. This method seems most robust of the ones that have been tried out; it gives values between a pure linear derivation, which underestimates the contact angle, and higher order (polynomial) methods that usually tend to overestimate the angle.

The third method is a straight line linear fit. As most drop profiles are not linear, this fit will underestimate the angle, and should only be used in special cases. These may be for instance the measurement of a straight edge (for calibration purposes) or very noisy data.

The curve fitting methods may be used when the entire drop profile is not visible; for instance the pipette method can be used for approaching/receding contact angles.

Measuring surface dilatational modules – a brief theoretical description.

The theoretical foundation for the measurement of surface rheological properties is well established (1,2). The analysis of surface dilatational elasticity and viscosity has for instance been reviewed by Lucassen-Reynders (3). In this framework the necessary theoretical background for the methods utilized in this work will be outlined below. The surface elasticity, E, follows the definition given by Gibbs,

$$E = \frac{d\gamma}{d\ln A} \qquad [18]$$

Here γ is the surface tension and A is the surface area. The term surface elasticity infers that E is a property of pure elastic surfaces. It turns out, however, that many surfaces both contain elastic and viscous components, and the term "surface dilatational modulus" has been used for this more general case. The contribution of the elastic and viscous terms depend on the different types of relaxation processes that occur in the surface layer and on the interaction of the surface with its surroundings, i.e. the bulk liquid(s). The equilibrium (Gibbs) surface elasticity, E_0, will then usually be different from E. The surface dilatational viscosity, η_d, has been defined according to the equation

$$\Delta\gamma = \eta_d \frac{d\ln A}{dt} \qquad [19]$$

where $\Delta\gamma$ is the surface tension difference of a constantly (logarithmically) expanding surface compared to that of the equilibrium surface. The parameter η_d will only represent true Newtonian types of surface viscosity, however, if the elasticity is zero. In other cases, a complex surface dilatational modulus may be written as

$$E^* = E' + iE'' \qquad [20]$$

where E' is the storage modulus and E" the loss modulus. The storage modulus will be equal to the pure elastic contribution, and E" proportional to the viscous contribution. In an oscillatory experiment the surface area is varied with time, t, according to the function

$$\Delta\ln A \sim \exp(i\omega t) \qquad [21]$$

where ω is the angular rate. In this case the loss modulus will be

$$E'' = \omega\eta_d \qquad [22]$$

and E' will be equal to E_0 when $\omega \rightarrow 0$. The surface dilatational viscosity, η_d, therefore corresponds to the dynamic viscosity, $\eta' = G''/\omega$, in an ordinary (bulk) oscillatory rheology experiment (G" is the bulk loss modulus). It is implied here that the surface area amplitude is sufficiently small to insure operation in the linear viscoelastic regime. The above analysis can be used with experiments such as surface waves and oscillating drops and bubbles. For an oscillating bubble, we vary the surface area according to Eq.[21] by pulsating the bubble volume in a sinusoidal manner, and provided that the volume change is small, this results in a corresponding sinusoidal variation in the bubble surface area:

$$\Delta A = A - A_0 = A_a \sin(\omega t) \qquad [23]$$

Here A_a is the area amplitude and A_0 is the equilibrium surface area. The response in the surface tension variation can then be described by the function

$$\Delta\gamma = \gamma - \gamma_0 = \gamma_a \sin(\omega t + \delta) \qquad [24]$$

where γ_a is the measured amplitude, γ_0 is the equilibrium surface tension and δ is the phase angle. In the usual manner, Eq.[24] may be written

$$\Delta\gamma = \gamma_a \sin(\omega t)\cos\delta + \gamma_a \cos(\omega t)\sin\delta \qquad [25]$$

By using Eq. [18] for E*, we see that the (complex) surface dilatational modulus is then expressed by

$$E^* = E' + iE'' = |E|\cos\delta + i|E|\sin\delta \qquad [26]$$

where

$$|E| = \frac{\gamma_a}{A_a / A_0} \qquad [27]$$

The loss modulus E" represent a combination of internal relaxation processes and relaxation due to transport of matter between the surface and the bulk. The latter process will be important especially in the case of soluble monolayers and in non-equilibrium situations, and will be more dominant at lower frequencies because of the time involved in the diffusion process. Several theories have been developed that describe the latter process (2,3), and it is predicted that in this case, the phase angle, δ, will be 45° and the elasticity will approach zero at low frequencies (3). The interested reader is referred to the above literature for in-depth discussion of this topic.

Often, the response function, Eq. [24] is determined from the experimental data by means of a Fourier transform. The transformed time function should ideally only contain the main harmonic component, however, noise in the experimental data will usually also give rise to higher, harmonics content, which may complicate the analysis. It will also be important to consider the boundary problem. Another method of analysis is to fit Eq. [24] directly to the experimental data. A non-linear curve fitting procedure is able to obtain the universally best results even from noisy data; it is, however, necessary to use good initial parameter estimates if this strategy will succeed. Such parameters may be obtained by pre-analyzing the data in a proper way. For the zero values (A_0, γ_0) the arithmetic means can be used, and the amplitudes (A_a, γ_a) may be calculated from the standard deviations when it is observed that, for a sine function

$$\text{Amplitude} = \sqrt{\frac{2}{N}\sum_{i=1}^{N} y_i^{\,2}} \qquad [28]$$

Here y_i are the experimental data and N the number of measurements. The frequency and phase angle relative to the start measurement time may be estimated by simply counting the data points below and above the mean in each period. By using these initial values in a non-linear least squares curve fitting procedure, it is usually quite easy to obtain a good fit of the sine function to experimental data. It should be stressed that this method for the determination of the surface dilatational modulus is based on the analysis of the drop image only, and that an additional determination of the capillary pressure as in earlier published methods is not necessary. This is so because the surface tension is determined from the bubble's shape (together with the size) and that the shape may change as a result of a surface pressure change even at constant surface area.

References

1. Edwards, D.A., Brenner, H., and Wasan, D.T., «Interfacial Transport Processes and Rheology», Butterworths-Heinemann Publishers, 1991.
2. Dhukin, S.S., Kretzschmar, G., and Miller, R., «Dynamics of Adsorption at Liquid Interfaces», Elsevier, 1995.
3. Lucassen-Reynders, E.H., «Surface Elasticity and Viscosity in Compression/Dilation», *Surfactant Science Series*, **11**, 173 (1991).

APPENDIX 2

INSTALLATION

To install the DROPimage Advanced program on a hard disk, please run the DropAdvSetup.exe file on the distribution Disk. The installation program puts a program icon on your desktop and also copies the program icon to the Ramehart Start menu group. It is recommended that the default installation directory c:\DropImage is used. If not, the default directories in the included methods and parameter files will be wrong, and must be changed before the program is started.

The program uses the Microsoft Windows installer. It the installer warns you that your installer has the wrong version; you do not need to worry, as the program contains the installer needed. Just select OK and the program will be installed.

The program is copy protected, and when started the first time, the program will show you a system number, and then ask for the registration number. You will have to contact ramé-hart to obtain the registration number. If you reinstall the program, or an update, on the same computer, the same registration number should be used.

If you want to uninstall the program and its files, select the Add or Remove programs icon in the Control Panel, select DROPimage Advanced and press Remove. The Uninstall program does not remove files that have been created after the program was installed, such as Method files, Parameter files, log-files etc. You have to remove these files manually.