

Instruction Manual for BI-9000AT Digital Autocorrelator

Windows 9KDL SW Versions 1.25 and Higher

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Please Read

This is your instruction manual for your Brookhaven BI-9000AT Digital Autocorrelator and 9KDLSW control program. Please read it carefully before making measurements. The **Installation** section, Section III, describes procedures for checking that the instrument and software are working properly *without an external signal input*. Familiarize yourself with the software by running the program with the built-in simulator. This you can do by working through **Section V: Quick Start** first. You can generate and save various simulated data sets, and you can calculate results to test your understanding of the operation of the software. The procedures described there are also very useful as an instructional aid for first-time correlator users. If you have a signal available we strongly recommend learning the program starting with **Section V: Quick Start**. If you have any questions or suggestions, please contact Brookhaven Instruments.

This program requires Windows 3.X or higher and 4 Mb of RAM, but we recommend at least 8 Mb.

Besides its use with the BI-200SM motorized goniometer, or any manual goniometer, this program can be used with the Brookhaven FOQELS, 90Plus, and with the BI-MAS option on either the ZetaPlus or ZetaPALS instruments. The FOQELS, 90Plus, and BI-MAS option are supplied with the 9KPSDW program, a dedicated particle sizing program that allows very limited control over the correlator. Correlation functions collected with the 9KPSDW program may be exported and saved for subsequent analysis using the 9KDLSW program, but not the other way around.

Software is never really finished: there are always additions and changes. As these become available, they will be added to the back of this manual as appendices. Please look at the appendices if you cannot find the answer to your questions in the main part.

Remember the old saying: “When in doubt, read the instruction manual.” Sometimes the solution to your problem has already been addressed. You just need to find it. Thanks for purchasing a Brookhaven.

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Warranty

Brookhaven Instruments Corporation (hereinafter known as BIC) warrants that the product is free from defective material and workmanship. Under the terms of this warranty BIC agrees to correct by repair, or at BIC's election, by replacement any parts which prove to be defective through no fault of the user.

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The BIC warranty extends for a period not exceeding the warranty period of the original equipment manufacturer where applicable. The typical warranty period on printers and computer peripherals is 90 days. Please contact BIC for copies of applicable OEM warranties.

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Carefully read the following terms before using the software provided with this system. Use of the software indicates your acceptance of these terms. If you do not agree with the terms, promptly return the software and system. BIC refers to Brookhaven Instruments Corporation.

Terms:

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Information produced by using this BIC software and its manual, including the resulting displays, reports, and plots, are believed to be accurate and reliable. However, no responsibility is assumed by Brookhaven Instruments Corporation for any changes, errors, or omissions.

Section I: Introduction

General Description

The BI-9000AT is an entirely digital, high speed, signal processor which can be used as an auto- or cross correlator for dynamic light scattering measurements (DLS) and as a photon counter for static light scattering measurements (SLS). It operates entirely in real-time at 100% efficiency over 10 decades in delay time. The correlator is located on one ISA-compatible card that fits into a PC (or pre-installed in a PC, depending on what you ordered). An option, the BI-CON stepping motor controller for use with the BI-200SM multiangle goniometer, is provided as a separate card.

BIC has written its correlator control program in C++, suitable for use with Windows 3.11 or higher. We recommend the use of at least 8 Mb of RAM and either a 100 Mhz 486 or Pentium™ PC. There is also a version running under DOS; however, there are many more features available in the Window's version. Contact the factory if you want a DOS version. Normally one is supplied on the hard disk drive, if you purchased the computer from Brookhaven. Just type BI9 from the BI subdirectory to invoke the DOS version, and order our BI-9KATMAN, VER 2.2 manual for a complete description of the DOS software.

The correlator control program described in this manual, 9KDLSW, is Windows-based and was designed for use with the BI-9000AT correlator and either the motorized BI-200SM goniometer or any manual goniometer used for research. The 9KDLSW may also be used to run the FOQELS, 90Plus, and the BI-MAS option in the ZetaPlus or ZetaPALS. However, the simpler 9KPSDW, a Windows-based program dedicated to particle sizing, is recommended for use with these dedicated instruments. The simpler program allows less control over the correlator and is thus easier to use. Very little operator interaction is required. The 9KPSDW is also available for use with the BI-9000AT. Contact the factory to order this program.

Windows Software Version

The Windows software is quite powerful with many new features not available in the DOS version, a few of which are:

- Resizable Windows and groups of Windows that can be saved and reloaded by name.
- A complete database management system by folders and files.
- Data logging to create a single file with a subset of the information from many files.
- Ability to design the number and type of printouts, including a preview feature.
- Simulated data that can be overlaid with real data.
- Overlay of up to 6 correlation functions, measured or simulated.
- Count rate history and distribution useful for determining stability or trends.
- Fourier transform of linearly spaced correlation functions.

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- Experiment duration as number of samples, total time, user settable difference between first delay time and baseline, or user settable difference between measured and calculated baselines.
- User designed correlator control window that may display the status of the traditional parameters such as first/last delay, samples, count rate, etc., as well as effective diameter, angle, dust cutoff, etc.
- Control of up to 8 correlator cards and 16 correlation functions with synchronized accumulation of data.
- Advanced, C-based scripting language allowing unlimited, unattended data collection with the ability to save and recall named scripts.
- Scaling both the X and Y axis as log or linear for correlation function graphs.
- Automatic update of size distribution graphs during the measurement.
- Automatic calculation of viscosity and refractive index as a function of temperature for several common liquids.
- User selectable baselines: calculated, measured, bound, autoslope.
- Zero to 8 extended channels, with user settable delay from two to 10 times the last contiguous channel.

Correlator Applications

The BI-9000AT is useful in a number of signal processing applications, especially those involving light scattering.

In the photon counting mode, it can be used to measure time-averaged scattered light intensity. This is called static light scattering (SLS). In dilute polymer solutions, this information can yield the molecular weight, radius of gyration, and the second virial coefficient—all useful parameters of the polymer and/or polymer/solvent interaction. The angular intensity pattern from suspensions of dilute aggregates such as gold sols, α -Fe₂O₃, and other colloidal particles can be made to yield the fractal number, a number characteristic of the type of growth that occurred. Full Mie theory, applied to the angular intensity pattern from monodisperse particles suspended in liquids, can yield a very accurate estimate of the size for particle sizes comparable to the wavelength of light. In general, SLS measurements lead to structure. Please ask for information on the BI-SLSW software.

In the autocorrelation mode, the 9000AT can be used for dynamic light scattering (DLS), also known as photon correlation spectroscopy (PCS). Light scattered from solutions of synthetic and natural macromolecules contains information on the dynamic and static properties of the macromolecules. These properties include translational and rotational diffusion coefficients, size, shape, molecular weight, intramolecular relaxation rates, and polydispersity. Measurement of this latter property makes the 9000AT particularly useful for measuring size distributions, especially for colloidal sized particles.

The correlation of scattered light can also be used to determine velocity. Known as laser Doppler velocimetry (LDV) or laser Doppler anemometry (LDA), applications in gas,

liquid and solid flows include the following types of measurements: mean velocity, root-mean-square turbulence (turbulence intensity) velocity distribution, and turbulence frequencies. Applications that can be found in the literature include measurements of streaming velocity in plant cells and swimming speed distributions in motile microorganisms as well as studies on jet engines in wind tunnels. Such measurements require special optics and, except for the correlator, detectors, and software, are not offered by Brookhaven as a system.

Electrophoretic light scattering (ELS), and the newer phase analysis light scattering (PALS) bridge the gap between DLS and LDV. While not based on autocorrelation, instrumentation for ELS (ZetaPlus) and PALS (ZetaPALS) measurements are available from Brookhaven. Such instruments are used to determine electrophoretic mobility and zeta potential from which the stability of dispersions may be determined.

Other light scattering applications for the instrument include the investigation of critical phenomena such as liquid-gas critical points, liquid-crystal phase transitions, micelle formation, binary and ternary liquid Plait points, tricritical points, and temperature-concentration phase diagrams of polymer solutions. Dynamic depolarization light scattering (DDLS) can shed light on particle shape and internal structure in special cases. Surface light scattering, a special form of DLS, has been used to study surface tension and surface viscosity. Such measurements require special optics and, except for the correlator, detectors, and software, are not offered by Brookhaven as a system.

In recent years the autocorrelation function (ACF) at two extremes of the delay time range has become interesting. At long delay times, tens of seconds and longer, the slow relaxation processes in gels, viscous liquids, concentrated colloidal suspensions, and concentrated polymer solutions are much studied as are glass transitions. Here the 16-bit multiplications and the sampling time scheme of the 9000AT are very useful. At short delay times (25 ns to 10 μ s) the fast decay times due to multiple scattering in highly concentrated suspensions are interpreted in terms of diffusing-wave spectroscopy theory, out of which particle size and other structure related parameters can sometimes be determined.

Specifications

The following list of standard and optional features applies to all units covered by the version number given in Section II. Special options, if any, are noted in Section II and documented in the appendices or as supplements to this manual.

BI-9000AT Correlator Specifications

Section	Channels	Sampling Time Range	Maximum Delay Time	Hardware Multiplier Bits
Low Speed	1 to 240 max	50 μ s to 40 ms	1,310 s (40 ms)	16 x 16
Mid Speed	1 to 256 max	500 ns to 100 μ s	1.6 s (100 μ s)	8 x 8
High Speed	14 standard and 12 optional (<i>bold italics</i>) channels fixed at: 25, 50, 75, 100, 125, 150, 175, 200, 225, 250, 275, 300, 325, 350, 375, 400, 500, 600, 700, 800 ns, 1.0, 1.2, 1.4, 1.6, 2.0, and 2.4 μ s			
Max Number Channels:	240 + 256 + 14 + 12 = 522			
Delay Time Axis:	User selectable (except fixed channels) from linear, constant ratio, or as individual time points recalled from user files by name.			
Dynamic Range:	Over 10 decades (1,310s/25ns).			
Operation Modes:	Automatic and Manual. With macro commands the user can write, save, and recall an unlimited number of automatic sequences initiated by a single keystroke.			
Maximum Count Rate:	40 Mcounts/s.			
Standard Input Levels:	TTL, 50 ohm input impedance, 5ns minimum pulse width. Other levels available via external converters.			
Power Requirements:	ISA-compatible Bus, 22 Watts/card, 12 Watts with Power Saver. Power Saver feature automatically removes power from unneeded, high speed channels.			
Physical Dimensions:	Full ISA-compatible Bus card, ~100 grams.			
Card Connectors:	Four co-axial Lemo connectors for inputs to the middle and low speed correlators; two 4-pin Lemo connectors for low voltage power to BIC detectors.			

Additional Specifications Include:

Functions:	Auto- and cross correlation.
Duration :	<ol style="list-style-type: none">1. Total time in minutes and seconds.2. Total number of samples.3. Specified difference in first channel and calculated baseline.4. Percent difference in measured and calculated baselines.
Extended Channels:	0 to 8, linearly spaced, from 2 to 10 times last delay time.
Measured Baselines	<ol style="list-style-type: none">1. Average of extended channels.2. Average of any consecutive group of channels up to 32.3. Autoslope: average of up to 32 consecutive channels when slope of first eight less than -0.0007 times amplitude of first channel.
Monitor Channels:	Record the following information: <ol style="list-style-type: none">1. Total number of samples.2. Total counts from Input A.3. Total counts from Input B in cross correlation or total counts from Input A in autocorrelation.4. The measured baseline (average of 1 to 8 extended channels, average of 1 to 32 autoslope channels, or average of 1 to 32 user-selected, consecutive channels.5. A calculated baseline determined from the number of samples and the total counts.6. A count rate updated every second.
Screen Scaling or Display Modes:	Linear or Logarithmic. Raw Data or Baseline Subtract, using either the calculated or measured baseline. Manual, auto, or exact scaling.
Data Collection:	Manual sequencing, saving to a file, and optional internal calculations. Complete and automatic control via scripting language.
Software :	Correlator control program, 9KDLSW, standard.
Options:	BI-25NS: Twelve, 25 ns channels.

BI-ANIN: Analogue input.

BI-CON: Stepping motor controller for use with BI-200SM goniometer and its accessories and may be used with most motorized goniometer.

BI-ISTW: Alignment/stability software for use with manual and motorized goniometers such as BI-200SM.

BI-PCSW: Simple particle sizing algorithm using first and second order cumulants.

BI-ISDAW: Advanced particle sizing algorithms: CONTIN, NNLS, Exp. Sampling, Double Exponential, 1st to 4th Order Cumulants, Williams-Watts.

BI-ZPW: Molecular weight algorithms: Zimm, Debye, Berry plots.

BI-SLSW: Particle and fluid structure algorithms: Guinier, Kratky, Fractal, R_g , $\ln(I)$ vs q .

BI-NT: Special drivers for WinTM NT, contact factory.

Section III: Installation

Installation

Computer Supplied By Brookhaven

Your BI-9000AT consists of the computer, keyboard, monitor, software, cables, manuals, and optional printer. The correlator board is installed in the computer and the software is installed on the hard disk. Examine the shipping containers for external damage. Carefully remove all items from the shipping containers. Pay particular attention to manuals and detachable power cords. If any damage is found, please contact the carrier and Brookhaven immediately. Make sure to save all packing materials and containers.

1. Remove the cover of the computer. Check for loose boards or connectors or any other sign of internal damage. Correct any obvious problems, or call your local sales office if the problems appear to me more serious. Replace the cover when finished.
2. Plug the keyboard and monitor into the appropriate connectors on the rear of the computer. These connectors are polarized and labeled, and they can only be inserted in one position.
3. Verify the voltage selector on your computer and monitor are set to the proper voltages. Plug the computer into an outlet and plug the monitor into the special outlet located on the back of the computer. [Some of the newer CE marked computers do not have power output capability, and the monitor must be plugged directly into an AC source.] Turn on the computer and monitor.
4. Verify that the Program Manager of Windows, or the equivalent in Windows 95, is displayed and that a BIC Window or icon is displayed labeled "BIC Dynamic Light Scattering Software". If the BIC window is not installed, do it now using the diskettes supplied. Follow the instructions on the diskette label. This software is installed like any other Windows-based program.
5. If you ordered a printer, follow the instructions in the printer manual to test the printer. Connect the printer to LPT1 of the computer using the appropriate cable.

Computer Not Supplied by Brookhaven

The BI-9000AT correlators live exclusively in I/O space and occupy ports 300H to 313H. **Verify** that no other boards in your computer use these port addresses. Standard computers that have COM ports, LPT ports, or floppy or hard disk controllers never use these ports. Special boards like analog-to-digital boards and network boards can create a conflict. If you have a board that conflicts with these ports, you must change its address to allow the Brookhaven boards to use these ports.

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There is no special procedure for installing a BI-9000AT correlator board into your computer. Simply install the board into either an eight bit or 16 bit slot and screw it down. Install the software by following the instructions on the diskette provided. The correlator board is a full sized card. Sometimes fans on CPU chips and extra memory (SIMM modules) get in the way. So choose a slot that is completely clear.

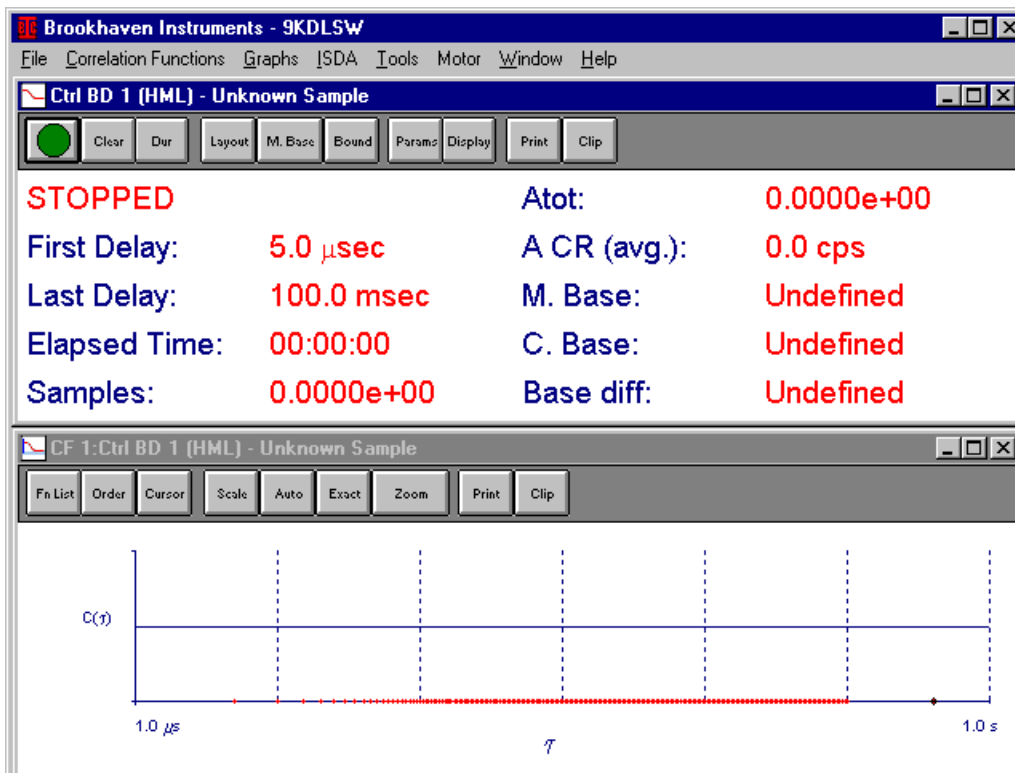
If you are installing the optional motor control board, make sure to connect a floppy disk drive power connector (4-pin, white Molex type, typically) to the four pin connector located on the top of the board. This connector is necessary to provide the power to the stepper motor.

Make sure Windows 3.X or Windows 95 is installed on your computer. Please test that it is working properly *before* installing the 9KDLSW software supplied on diskette. If you purchased the optional BI-ISDAW particle sizing software, install the diskette (labeled 9KDLSW/ISDAW) **after** you install the main 9KDLSW control program.

Testing the BI-9000AT

Double click on the BIC Logo, the one labeled Dynamic Light Scattering Software.

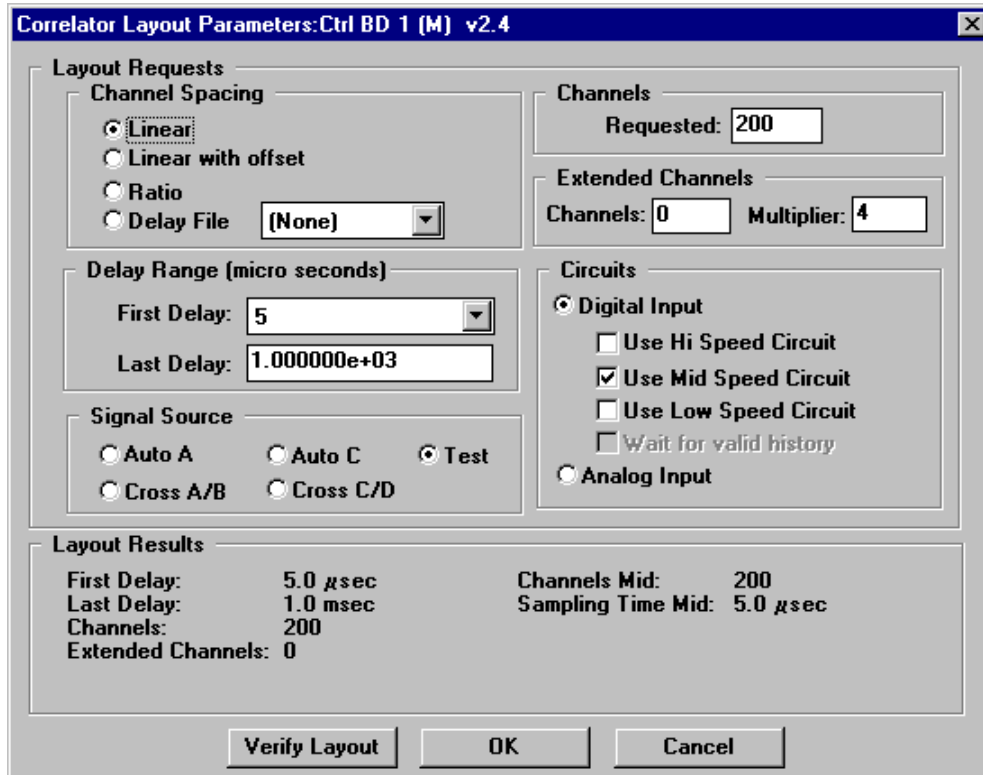
An image similar to the following should be visible on your screen.



If you do not see the default configuration as shown above, click on File. Then click on Restore Default Configuration.

The following tests use a signal generated internally and do not require an external signal attached to the correlator board.

To test the middle speed circuit, you must now layout the channels appropriately. Click on the Layout button in the Tool Bar corresponding to the control window, the top window in the display above. The following display appears.

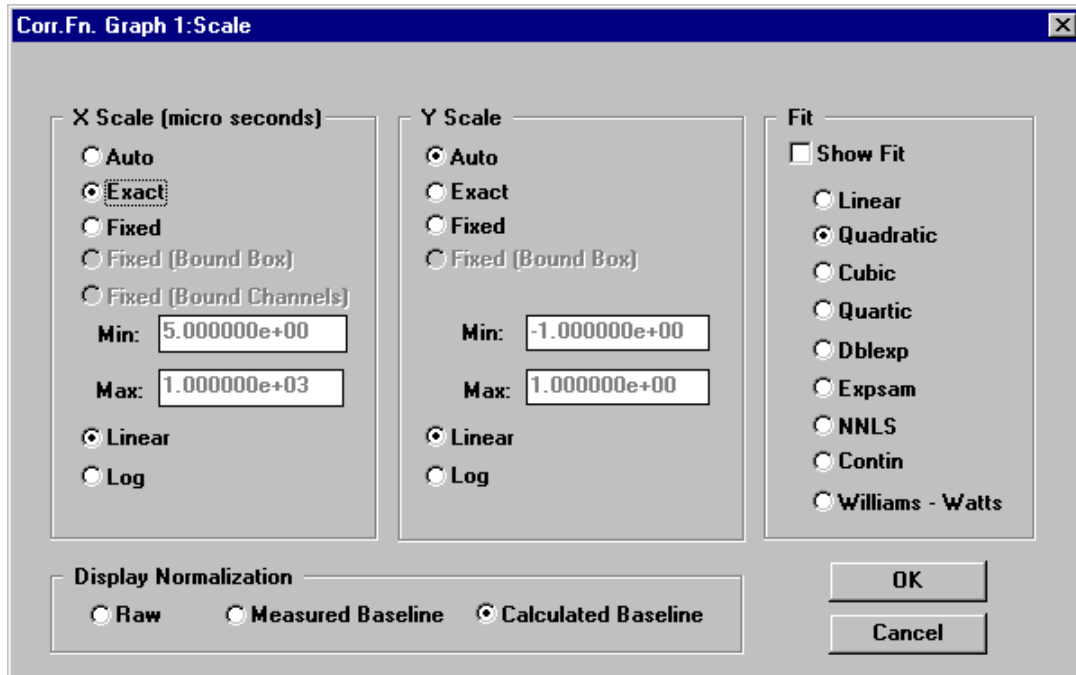


Set the following values as shown above:

- Linear spacing in the Channel Spacing Section;
- First Delay 5 μ s ; Last Delay 1,000 μ s in the Delay Range Section;
- Test in the Signal Source Section;
- Channels 200 in the Channels Section;
- Channels 0 in the Extended Channels Section;
- Use Mid Speed Circuit in the Circuits Section;
- And Test in the Signal Source Section.

Click Verify Layout and see that the values in the Layout Results match those in the display shown above. Click OK to return to the main display.

Next, in order to layout the correlation function graph for the middle speed circuit test, click on the Scale button in the Tool Bar corresponding to the correlation function window, the bottom window in the default configuration . The following display appears.

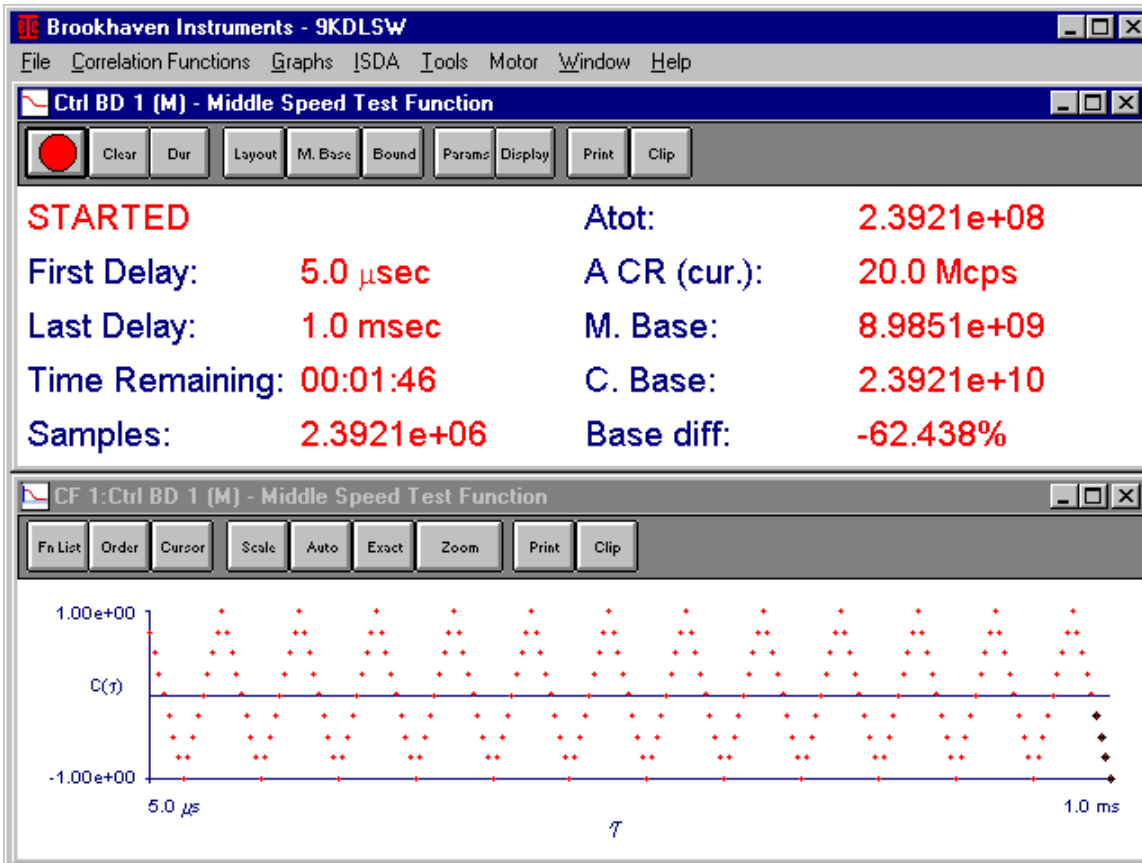


Set the following values as shown above:

- Exact and Linear in the X Scale Section
- Auto and Linear in the Y Scale Section
- All other settings are not significant for the test.

Click OK to return to the main display.

Click on the Start button (large Green icon) and within seconds you should see the triangular wave pattern shown below, indicating the middle speed circuit is functioning properly. If you do not see the pattern as shown here, click the Stop button (large Red icon). Then click on the Print button in the graph window. Contact the factory and be prepared to describe the pattern you have just printed.



Click on the Clear button in the control window.

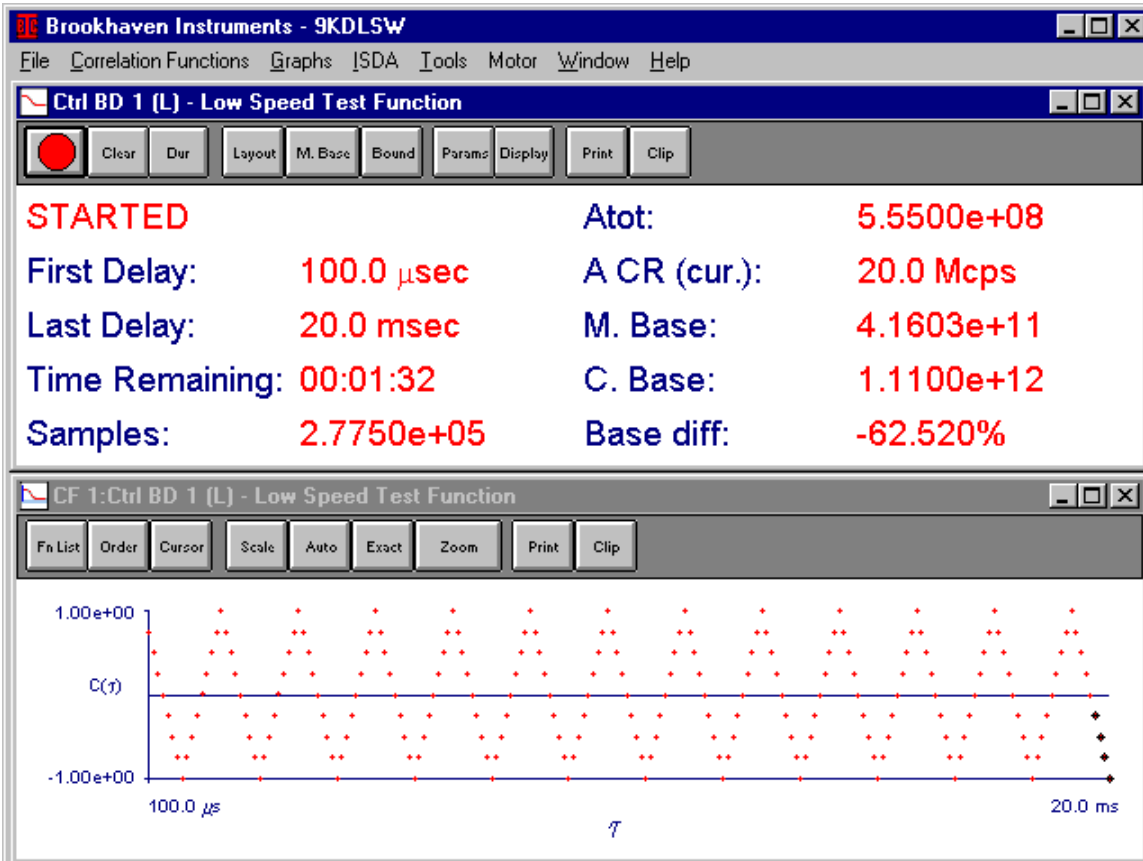
To test the low speed circuit, you must now change the channel layout appropriately. Click on the Layout button in the Tool Bar corresponding to the control window. The Correlator Layout Parameters window appears as before.

Make the following changes:

- Change the First Delay from 5 to 100 μ s;
- Change the Last Delay from 1 E3 to 20 E3 μ s;
- Click on the Use Mid Speed Circuit check box to unselect it;
- Click on the Low Speed Circuit check box to select it.

Click Verify Layout and see that the values in the Layout Results match those described above. Click OK to return to the main display.

Click on the Start button (large Green icon) and within seconds you should see the triangular wave pattern shown below, indicating the low speed circuit is functioning properly. If you do not see the pattern as shown here, click the Stop button (large Red icon). Then click on the Print button in the graph window. Contact the factory and be prepared to describe the pattern you have just printed.



If both patterns are okay, then both the middle and low speed circuits of the correlator are working.

Print Test

Click on the Print button in either of the Tool Bars. The printed results will indicate if your printer, cable, and software are working together.

Measuring A Signal

This section of the installation procedure takes you through the operations necessary to verify that you can measure an external signal. It is assumed that you have a detector with TTL outputs. In many cases this signal will come from the PMT on the BI-200SM goniometer.

The goniometer does not have to be completely aligned to make these checks. It should, however, be assembled to the point where a signal can be generated. (See the BI-200SM manual.)

[If you are using the FOQELS, the 90Plus, or the BI-MAS option on either the ZetaPlus or ZetaPALS, most of the following steps are either not necessary or not convenient. Instead, just click on the Start icon with a sample inserted into the instrument. Record the A CR (avg). This is the average count rate for input A. Click on the Stop icon. Dilute the sample by approximately half. Click on the Clear button. Then click on the Start icon. The A CR (avg) should be approximately one half its previous value.]

1. **Do not turn on the high voltage** or the correlator at this time.
2. Check the logic levels. The BI-9000AT requires TTL pulses. If you received the 9000AT and a BIC detector or goniometer, then the matching levels are TTL. If you are updating your correlator from a 2020, 2030, 2030AT or 8000AT check the USER CONFIGURATION sections of the manuals supplied with the detector and/or goniometer. Typically, the matching levels in these older systems were either ECL or something close to ECL, occasionally TTL or NIM. **Connecting the wrong levels may cause damage.** Check. Universal level shifters are available from the factory, or the pulse amplifier/discriminator inside the PMT housing can be upgraded.

[Note: The output levels in the FOQELS, 90Plus, ZetaPlus, and ZetaPALS are already set for TTL output.]

3. Connect the signal from the output of the detector system to INPUT A on the correlator. The BI-9000AT requires a special, mini LEMO connector for the inputs. Make sure you have the correct cable. The connector for the signal output on the rear of the PMT housing is a BNC type. A cable with appropriate connectors is supplied by Brookhaven when you purchase the correlator.

[Note: A coaxial cable is supplied with a mini LEMO connector on one end and a BNC on the other for the FOQELS, 90Plus, ZetaPlus, and ZetaPALS. In the last three instruments mentioned, the cable is approximately 30 cm long and should be attached to the appropriate connectors on the rear panel of the instrument. See the manual that comes with each of those instruments.]

4. Connect the low voltage output on the rear of the correlator to the input on the rear of the PMT housing. There are two low voltage outputs on the correlator. Use either one.

Both are just below the four inputs. The input on the rear of the PMT housing is marked either LV or J3. The cable has a 4-pin LEMO connector on one end and a 4-pin, half-moon LEMO connector on the other.

[NOTE: For older systems, the ones with the HV ***not*** mounted on the detector rail, connect the cable directly to the rear of the PMT housing. For newer systems, the ones with the HV mounted on the detector rail, connect the cable to the LV In connector on the small, black HV. Connect the LV Out on the HV to the LV or J3 connector on the rear of the PMT.]

5. If the logic levels are matched and the cable is connected correctly, turn on the computer. Double click on the BIC Dynamic Light Scattering Software icon to start the program.

Click on the button labeled Dur in the control window. It stands for experiment *duration*. There are four ways to set the duration, but for purposes of the installation just use the one for total time. Click on the radio button labeled “Elapsed Time”, if it is not already black. Click on the down arrow next to the “Minutes” box until the value is zero. Click on the up arrow button next to the “Seconds” box until the value is 10 seconds. Click on Ok to accept your selection and return to the main display.

Click the Start icon. With no high voltage attached you should see zero counts. The counts are displayed in the upper right section of the top window next to the label “Atot”. If counts are registered, contact the factory for advice. After 10 seconds the collection of data stops automatically. To stop earlier, click the Stop icon. Click on the Clear button.

[Note: If you have the FOQELS, 90Plus, ZetaPlus, or ZetaPALS you will register counts even without a sample, because the HV is always on. You are measuring dark counts.]

6. With the HV switched off, connect the high voltage power supply to the HV connector on the rear of the detector system. The connectors are both MHV types (mini high voltage). The exact HV setting was factory preset to correspond to the PMT selected for use with your BI-200SM.
7. Turn off the room lights. Block the laser beam with the mechanical shutter. Set the filter wheel to a closed positions. It is marked C.
8. Turn on the HV. Click the Start icon. Divide the counts obtained by 10. This is the dark count *rate* in cps, counts/second. See the USER CONFIGURATION page in the BI-200SM manual for the dark count rate obtained at the factory. Dark count rates vary from a few tens of counts per second to a few hundreds of counts per second.

[NOTE: Since dark count rates are typically low, the repeatability is expected to be low (Poisson statistics). In addition, the dark count rate is temperature sensitive, typically doubling for every 10 °C temperature rise in room temperature.]

9. Turn on the room light. Measure the dark count rate again. The dark count rate should not increase, on average. If it does, check for light leaks around the detector system. Reseat the detector optics or the PMT housing. **Do this with the HV off.** Then recheck the dark count rate again with the lights on and off.
10. If the PMT is mounted on the goniometer, turn the filter wheel to the wavelength of the laser you will be using. Measure the count rate obtained with the room lights on. They should be the same, possibly a little higher depending on the aperture setting. The 100, 200, and 400 micron settings will result in little, if any,
11. additional light reaching the PMT. The 1, 2, and 3 millimeter settings may, depending on the lighting conditions in the room, show a few hundred counts more, possibly as many as a few thousand more counts per second.
12. Turn on the laser and provide a scatterer. Typically, the index matching liquid is sufficient for this purpose. Measure the count rate. With the aperture wheel set to 2 millimeters, the count rate from a pure liquid should be tens of thousands of counts per second, or more (it depends on the laser power). With a strong scatterer it may be a few megacounts/second. Reduce the laser power or the particle concentration until the count rate is less than 1 Mcount/s.
13. Set the aperture wheel to 1 mm. The rate should drop by approximately the ratio of the areas of the apertures, 1/4 in this case.

[NOTE: If you do not have a laser for this final test, you can use the room light; however, be exceedingly careful not to expose the PMT to direct light. Use the diffuse reflectance off the lab walls. Make sure to start with the 100 micron pinhole. Switch to larger diameter apertures only after measuring the count rate at a smaller one. NEVER EXCEED approximately 5 million counts per second.]

Contact the factory if you have any problems.

Congratulations

Your system is installed.

- The computer works.
- The program can be executed.
- You can print out results.
- You can measure intensities.
- You have measured your dark count rate and checked that the system is sensitive to variations in light.

One last piece of advice:

MAKE FREQUENT COPIES OF YOUR DATA FILES

If any of the hardware fails Brookhaven Instruments can repair it. If any of the programs are corrupted or lost, we can send you copies. We cannot, however, recover your lost data files. That is your responsibility. After all, that distorted looking correlation function may turn out to be the founding piece of evidence in a new branch of polymer physics: if only you had a copy of it.

Section IV: Theory of Operation

Correlation

Correlation is a measure of the similarity between two quantities. In the time domain it is useful, among other things, for establishing correlation between random signals and for establishing periodicity in the presence of noise. The correlation between two signals $A(t)$ and $B(t)$ is defined as:

$$G(\tau) = \lim_{T \rightarrow \infty} \frac{1}{T} \int_{t_0}^{t_0+T} A(t) \cdot B(t - \tau) dt$$

T is the integration time; t_0 is the initial time; τ is a shift in time; $A(t)$ and $B(t)$ are the amplitudes of the time-varying signals; and $G(\tau)$ is called the cross correlation function. A correlation function is a plot of $G(\tau)$ versus τ , where τ is called the shift time, the delay time, or the lag time. In this manual we prefer to use the term delay time.

If $A(t)$ and $B(t)$ are the same function, that is $B(t-\tau)$ is simply a delayed version of $A(t)$, then $G(\tau)$ is called the autocorrelation function, abbreviated ACF. The Fourier transforms of the autocorrelation and cross correlation functions are the power spectral density and the cross power spectral density functions, respectively. As such, they contain, in principle, information in the frequency domain equivalent to the information the correlation functions contain in the time domain.

For stationary signals (signals independent of the initial time) and for ergodic systems (systems in which the time averages are equivalent to ensemble averages), the correlation function can be written as

$$G(\tau) = \langle A(0) \cdot B(\tau) \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_{t_0}^{t_0+T} A(t) \cdot B(t - \tau) dt$$

where $\langle A(0) \cdot B(\tau) \rangle$ is the ensemble average.

The cross or autocorrelation functions may be obtained with analog processing by multiplying the signal $A(t)$ with a delayed version of signal $B(t)$ or itself, $A(t-\tau)$, and averaging this product over T seconds using, for example, an RC or operational amplifier integrator. However, analog integration can lead to distortion in the measured function. Because of the advances in digital electronics, and since some important time varying signals are discrete by nature (photons, for example), it is useful to approximate the integral by a finite sum of N products obtained by sampling the signal in discrete intervals. This sampling time (occasionally called the bin time) is designated as $\Delta\tau$.

In linearly-spaced correlators, the delay time is an integer multiple of the sampling time. The last delay time equals the sampling time multiplied by the number of hardware

channels. Because of the proportionality between the delay and the sampling times, these terms were often, and erroneously, used interchangeably. Sometimes the term sample time was used, even though such use is confusing and incorrect.

In the BI-9000AT the delay time and the sampling time are de-coupled. Furthermore, up to 4 different sampling times are possible: 25 ns and 100 ns in the high speed (HS) section; and two variable sampling times, one for the middle speed (MS) and one for the low speed (LS) sections of the correlator.

When approximating the ACF by a sum of N products, also called the number of samples, the ACF is written as:

$$G(\tau_j) = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{i=1}^N n_i \cdot n_{i-j} \quad j = 1, 2, 3 \dots M \quad ,$$

where τ_j is the j^{th} delay time, n_i is the number of pulses during the sampling time $\Delta\tau$ centered at some time t , n_{i-j} is the number of pulses during $\Delta\tau$ centered at $t-\tau_j$, and M is the number of correlator channels.

Multiplications

If the average count rate is designated $\langle CR \rangle$, then the average number of pulses, $\langle n \rangle$, in a sampling time is given by $\langle CR \rangle \cdot \Delta\tau$. For example, if $\langle CR \rangle = 200,000$ counts/second = 200 kcps, and the sampling time is 10 μs , then $\langle n \rangle = 2$.

The ability to form the complete product when multiplying pulses is limited by the number of bits the correlator provides. In the BI-9000AT the maximum sampling time is 40 ms: in this limit the number of bits is 16. Therefore, the maximum count rate, MCR, in this limit is $(2^{16} - 1)/40 \text{ ms} = 1.6384 \text{ Mcps}$. However, this limit exists only when the maximum delay time is set higher than 655.36 s. Between 327.68 and 655.36 s, a 20 ms sampling time is used, allowing a MCR of 3.28 Mcps. See Table IV-1c for more details.

The maximum sampling time in the MS section of the correlator is 100 μs . The number of bits in this section is 8. Therefore, the MCR for the MS section is $(2^8 - 1)/100 \mu\text{s} = 2.55 \text{ Mcps}$. Again, this is a limiting case. It is much more likely that a 5 or 10 μs sampling time will be used in the MS section, resulting in a MCR of 40 and 25.5 Mcps, respectively, where the upper limit of 40 Mcps is the limit imposed by the derandomizer circuits.

In the other limit, at 25 ns, the number of bits is 1. Therefore, the MCR is $(2^1 - 1)/25 \text{ ns} = 40 \text{ Mcps}$. This value also matches the limit imposed by the derandomizer circuitry. No more than 1 pulse per 25 ns can be counted using the BI-9000AT.

Furthermore, none of these calculated maximum values are really limiting when compared to the normal scattering rates and limits provided by detector electronics.

Dead-times for PMTs and associated amplifier/discriminator circuitry vary from roughly 10 ns to 50 ns. Based on these figures alone, MCRs without distortions vary from 2 to 10 Mcps. Normal scattering rates vary from a few kcps up to a few hundred kcps. At worst, if a local oscillator is used, it may add a few Mcps to the signal. Therefore, limits imposed by the BI-9000AT are almost never exceeded in practice.

Channel Layout

Delay times τ , sampling times $\Delta\tau$, multiplication (Bits), maximum count rate MCR, maximum delay times τ_{max} , and maximum number of channels N_{max} are shown for the three sections of the correlator in Table IV-1.

Table IV-1

A. High Speed (HS) Section, Fixed Delay Times

τ	$\Delta\tau$	Bits	MCR
25 ns	25 ns	1 x 1	40 Mcps*
50	25	1 x 1	40
75	25	1 x 1	40
100	25	1 x 1	40
125	25	1 x 1	40
150	25	1 x 1	40
175	25	1 x 1	40
200	25	1 x 1	40
225	25	1 x 1	40
250	25	1 x 1	40
275	25	1 x 1	40
300	25	1 x 1	40
325	25	1 x 1	40
350	25	1 x 1	40
375	25	1 x 1	40
400	25	1 x 1	40
500	100	2 x 2	30
600	100	2 x 2	30
700	100	2 x 2	30
800	100	2 x 2	30
1 μ s	100	2 x 2	30
1.2	100	2 x 2	30
1.4	100	2 x 2	30
1.6	100	2 x 2	30
2.0	100	2 x 2	30
2.4	100	2 x 2	30

*Note: The derandomizer places an upper limit of 40 Mcps.

The 12 delay times in bold are optional: 25, 50, 75, 125, 150, 175, 225, 250, 275, 325, 350, and 375 ns.

The MCR is equal to the lesser of 40 Mcps or $(2^n - 1)/\Delta\tau$, where n is the number of bits (here 1 or 2).

B. Middle Speed (MS) Section, Variable Number of Channels, N

$\Delta\tau$	Bits	MCR	τ_{\max}	N_{\max}
500 ns	8 x 8	40 Mcps	8.192 ms	20
1 μ s	8 x 8	40	16.384	40
2	8 x 8	40	32.768	80
5	8 x 8	40	81.920	200
10	8 x 8	25.5	163.840	256
20	8 x 8	12.75	327.680	256
50	8 x 8	5.1	819.200	256
100	8 x 8	2.55	1.638375 s	256

$MCR = (2^8 - 1) / \Delta\tau$, or 40 Mcps, whichever is smaller.

Note: In most circumstances $\Delta\tau$ for the MS section is 5 or 10 μ s, resulting in a MCR of 40 or 25.5 Mcps, respectively.

N_{\max} is the maximum number of channels allowed at a particular sampling time. This number includes any extended baseline channels. The maximum allowed by the software is 256 in the MS section.

τ_{\max} is the last delay time that can be reached using the sampling time shown.

C. Low speed (LS) Section, Variable Number of Channels, N

$\Delta\tau$	Bits	MCR	τ_{\max}	N_{\max}
50 μs	16 x 16	40 Mcps	1.638375 s	120
100	16 x 16	40	3.2768	240
200	16 x 16	40	6.5536	240
500	16 x 16	40	16.38375	240
1 ms	16 x 16	40	32.768	240
2	16 x 16	32.7675	65.536	240
5	16 x 16	13.107	163.8375	240
10	16 x 16	6.5535	327.68	240
20	16 x 16	3.27675	655.36	240
40	16 x 16	1.638375	1,310.72	240

$$\text{MCR} = (2^{16} - 1)/\Delta\tau$$

N_{\max} is the maximum number of channels allowed at a particular sampling time. The maximum allowed by the software is 240.

Note: When combining MS and LS circuits, the maximum total number of channels is 496. Adding 14 standard HS channels yields 510. Adding 12 optional HS channels yields 522.

τ_{\max} is the last delay time that can be reached using the sampling time shown.

Examples of Channel Layouts

General Description

Using this hardware one can make a linear correlator. For example, with $N_r = 100$ (*requested* number of channels) and $\tau_f = 5 \mu\text{s}$ (first delay time), the layout is 5, 10, 15, ... 490, 495, 500 μs . Or, one can make a nonlinear correlator with ratio R between adjacent channels. For example, with $N_r = 10$, $R = 2$, and $\tau_f = 5 \mu\text{s}$, the layout is 5, 10, 20, 40, 80, 160, 320, 640, 1280, and 2560 μs . Channels have to be integer multiples of the sampling time, in these examples $\Delta\tau = 5 \mu\text{s}$.

In the BI-9000AT the ratio is calculated from the first and last variable delay times, τ_f and τ_L , and from the requested number of channels:

$$\tau_f = \tau_L \cdot R^{N_r - 1} \quad .$$

The R calculated from this formula is most often not an integer. In this case each channel is selected as the nearest integer multiple of $\Delta\tau$. In other words, the delay times are calculated as follows:

where $i = 1, 2, 3 \dots N_r$ and $\tau_c(i)$ is the i^{th} calculated delay time. The actual delay time, τ , is then rounded to the $\tau_f = \tau_L \cdot R^{N_r-1} \pmod{\Delta\tau}$ nearest integer multiple of the sampling time.

To illustrate these rules, some examples follow. In these examples “ i ” is an integer used for counting, $\tau_c(i)$ and τ are defined above, N_a is the assigned channel number, and R_c is the calculated ratio of adjacent channels.

R Large

When R is large, all the requested channels are possible. R is large if N_r is small and/or the delay time range is large. For example, if $N_r = 15$, $\tau_f = 5 \mu\text{s}$, and $\tau_L = 5,000 \mu\text{s}$, then $\Delta\tau$ is automatically selected by the correlator as $5 \mu\text{s}$, and R is calculated as follows:

$$R = \exp[14^{-1} \cdot \ln(1000)] = 1.6379$$

i	$\tau_c(i)$	τ	N_a	R_c
1	5 μs	5 μs	1	--
2	8.2	10	2	2.00
3	13.4	15	3	1.50
4	22.0	20	4	1.33
5	36.0	35	5	1.75
6	58.9	60	6	1.71
7	96.5	95	7	1.58
8	158.1	160	8	1.68
9	259.0	260	9	1.63
10	424.2	425	10	1.63
11	694.8	695	11	1.64
12	1137.9	1140	12	1.64
13	1863.8	1865	13	1.64
14	3052.7	3055	14	1.64
15	5000.0	5000	15	1.64

Notice that the first four channels are linearly spaced. This is a direct consequence of delay times being integer multiples of the sampling time. Only in the case of *very* large R can this configuration be avoided. Notice also that R_c approaches the true ratio R .

The actual delay times τ are obtained from the calculated delay times τ_c by rounding to the nearest integer multiple of the sampling time $\Delta\tau$. In this example all requested channels are possible, and, as a result, the total number of assigned channels are equal to

the total number of requested channels. This is not always the case. Whenever R is small, rounding to the nearest multiple of $\Delta\tau$ will produce many replicate delay times. The replicates are dropped, producing an interim number of channels less than the requested number. Here is an example.

R Small

For example, if $N_r = 25$, $\tau_f = 5 \mu s$, and $\tau_L = 5,000 \mu s$, then $\Delta\tau$ is automatically selected by the correlator as $5 \mu s$. If the calculation were carried through as above, R would be:

$$R = \exp[24^{-1} \cdot \ln(1000)] = 1.3335$$

i	$\tau_c(i)$	τ	N_a	R_c
1	5 μs	5 μs	1	--
2	6.6	--	--	--
3	8.9	10	2	2.00
4	11.9	--	--	--
5	15.8	15	3	1.50
6	21.1	20	4	1.33
7	28.1	30	5	1.50
8	37.4	35	6	1.17
9	50.0	50	7	1.43
.
.
.
20	1185.7	1185	18	1.33
21	1581.1	1580	19	1.33
22	2108.5	2110	20	1.33
23	2811.7	2810	21	1.33
24	3749.5	3750	22	1.33
25	5000.0	5000	23	1.33

Of the 25 requested channels, 2 were replicates. Therefore, N_p , the number of possible channels is 23. When N_r is large and the delay time range is no more than a few decades, then the number of replicates will be large and N_p will be substantially less than N_r . In order to avoid this situation, where $N_p < N_r$, the program proceeds through a variety possibilities, depending on the layout requested, until $N_p = N_r$ or is as close as possible maintaining the hardware restrictions imposed by the correlator. To do this, the initial calculation of R proceeds with twice the number of requested channels, determines an initial N_p , and then iterates. In all cases the actual channel layout is available from the **Layout** command button in the correlator control window, and it is also available,

channel-by-channel, using the **Cursor** command button in the correlation function graph window.

Baseline Channels

There are two methods for normalizing the correlation function: calculated and measured baseline.

The calculated baseline, also called the infinite-time baseline, is obtained from the total pulses registered at the A and B inputs, A_{tot} and B_{tot} , and the number of samples, N_s . (In the case of autocorrelation $A_{tot} = B_{tot}$.) The relationship is:

$$\text{Calculated Baseline} = A_{tot} \bullet B_{tot} \div N_s$$

The measured baseline is the average of a group of channels, including a group of one if only one channel is selected. This group may be M channels extended beyond τ_L , or it may be an average of L adjacent channels anywhere between τ_f and τ_L . Whereas the M extended channels must be designated before the measurement is made in the *Layout* window, the L channels may be selected after the measurement using a *Bound Box*. M can be from 0 to 8, where 0 indicates no extended channels. L can be from 0 to 32. There is also an *Autoslope* feature for the measured baseline and it is described later in the manual.

The delay time of the last of the M extended baseline channels is selectable from 2 to 10 times τ_L . This may affect the sampling time necessary to reach such a long delay time. For example, if $\tau_f = 5 \mu s$ and $\tau_L = 50 ms$, then, without extended baseline channels, the entire function fits within the MS section of the correlator and $\Delta\tau_{MS} = 5 \mu s$. With extended baseline channels and the lowest multiplier of 2, the last of the M channels is at $50 \times 2 = 100 ms$, and this requires the use of the LS section with $\Delta\tau_{LS} = 50 \mu s$. (See Sections B & C of Table IV-1.)

Summary

In the following sections you will learn how to operate the correlator in order to implement the theory described in this section. Before you read those sections, it is worthwhile summarizing how the above theory works in practice.

The user selects the first and last delay times, linear or ratio spacing, any extended baseline channels, an extended baseline multiplier, and requests a number of channels. Given these user inputs the program automatically selects the sampling time or times, whether a single section (MS or LS) is sufficient or whether both are required to span the full delay time range. In ratio mode R is calculated. The possible number of channels is determined. All this information is displayed in the *Layout* screen (except R) and is part of any data file.

The examples described in this section are implemented automatically upon selection of the parameters just mentioned. There is, however, another way for a user to select a channel layout in order to override the automatic choices: delay time files. These are described in an appendix.

Section V: Quick Start

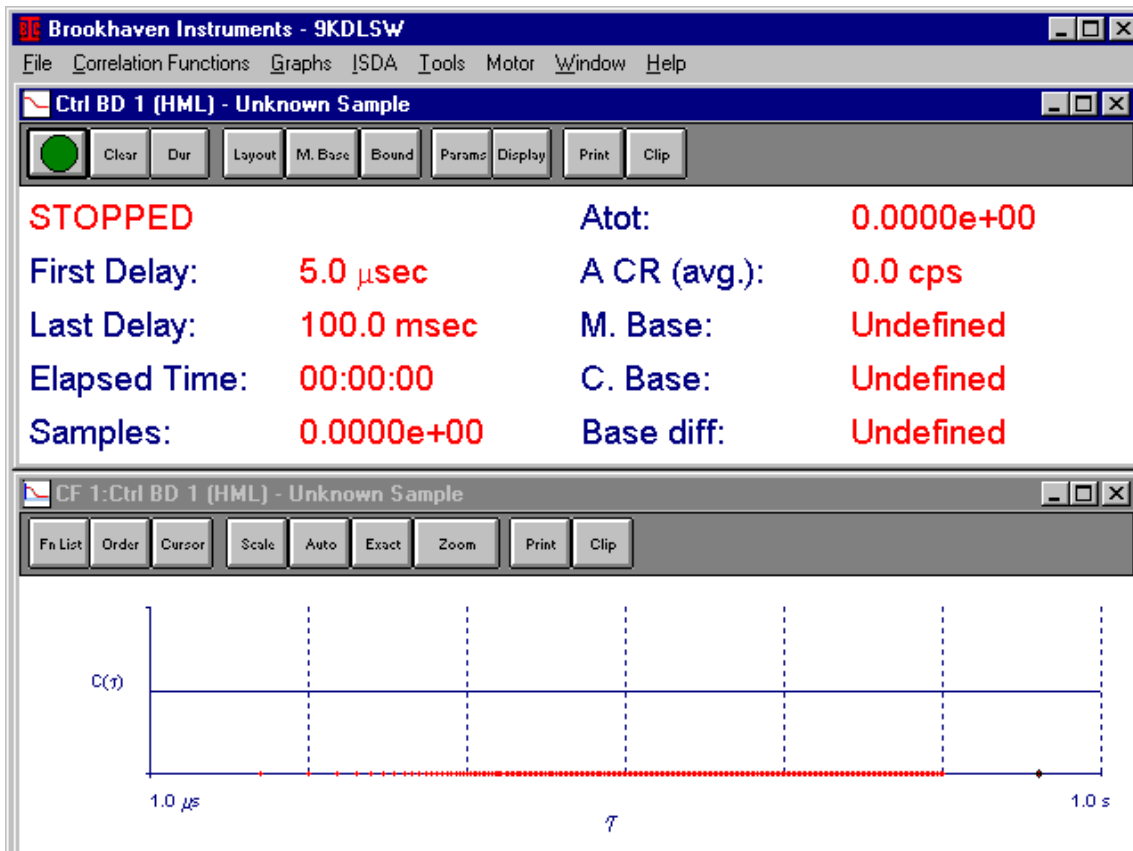
Getting Started

A general overview of the program is presented in this chapter. It is assumed that the correlator is attached to the Brookhaven BI-200SM goniometer and that you are interested in particle sizing. However, the presentation here is easily generalized. In this chapter many of the details are skipped over in favor of giving you an overview of often-used features. Further details are given in the following chapters, but here the emphasis is on getting you started.

Double click on the BIC icon labeled Dynamic Light Scattering in the BIC group window. If you installed the program for use with more than one instrument, click on BI-9000AT when the window with the list of instruments appears.

Default Configuration

The Default Configuration shown below should appear on your screen. If it does not, click on *File* in the main window menubar and then on *Restore Default Configuration*. The upper window is the correlator control window, labeled Ctrl BD 1, which indicates it is used to control correlator board number one. The program can control up to eight correlator boards simultaneously. The lower window is the associated correlation function graph (CF 1).



Click on *Motor* in the main window menubar. Set the current angle and the destination angle. In this example the destination angle is 90°. When you click on the *OK* button, the detector arm will move to the destination angle. You can change angles in this window or from the *Params* window.

Parameter Settings

In the correlator control window, click on the command button labeled *Params*. The window below appears. Enter a sample and operator ID, and any notes you find helpful. The sample ID is used in the title bar of any windows associated with the correlation function and in the database description.

The screenshot shows a dialog box titled "Calculation Parameters: Ctrl BD 1 (HML)". It contains the following fields and options:

- Sample ID: Broad PS/H2O
- Operator ID: D. Nicoli
- Notes: 10 mM NaNO3, sonicated
- Temp.: 25.0 deg. C
- Liquid: Aqueous (dropdown menu)
- Viscosity: 0.890 cP
- Ref. Index: 1.331
- Angle: 90.00
- Wavelength: 632.8 nm
- Refractive Index of Particles: Real 1.590, Imaginary 0.000
- Normalization: Calculated Baseline, Measured Baseline
- First Calc. Channel: 1
- Use Dust Filter
- Dust Cutoff: 50.00
- Measurement Type: Homodyne, Self-Beating

Buttons for "OK" and "Cancel" are located at the bottom of the dialog.

Enter the temperature of the sample. Click on the down arrow to the right of the box labeled *Liquid*. If the liquid for the continuous medium is listed, click on it and the refractive index and viscosity are automatically calculated for the entered temperature. If the liquid is not listed, or if you wish to override the automatic calculations, select "*Unspecified*" at the top of the list and enter the refractive index and viscosity manually.

Enter the wavelength of the laser. The refractive index will vary slightly with wavelength and temperature for each of the liquids listed.

Enter the real and imaginary parts of the particles refractive index, if they are known. For the intensity weighting that is recommended, the particle's refractive index is not necessary, but it will change results calculated with volume or number weighting.

Click on the box next to M to select normalization using the measured baseline. The final results depend on the choice of baseline, unless the calculated (C) and measured (M) baselines agree to ~0.1% or better. M is normally preferred to suppress the effects of any residual dust.

In the box for the channel number used for calculations, enter the number 1 for first delay times greater than 2 μs and 2 or higher for first delay times less than 1 μs , to avoid calculations that include afterpulsing effects associated with photomultiplier tubes.

Do **not** click in the box labeled *Homodyne*. **Do** click in the box labeled *Self Beating*.

Do **not** click on the *Use Dust Filter* check box if it is empty; do click on it to deselect it if it has a check mark.

Channel Layout

Click on the command button labeled *Layout* in the correlator control window.

Correlator Setup Parameters: Simulation 1

Layout Requests

Channel Spacing

Linear

Linear with offset

Ratio

Delay File [None] ▾

Channels

Requested: 200

Extended Channels

Channels: 8 Multiplier: 2

Delay Range (micro seconds)

First Delay: 5 ▾

Last Delay: 1.000000e+04

Signal Source

Auto A Auto C Test

Cross A/B Cross C/D

Circuits

Digital Input

Use Hi Speed Circuit

Use Mid Speed Circuit

Use Low Speed Circuit

Wait for valid history

Analog Input

Layout Results

First Delay: 5.0 μsec Channels Mid: 200

Last Delay: 10.0 msec Sampling Time Mid: 5.0 μsec

Channels: 200

Extended Channels: 8

Extended Last Delay: 20.0 msec

Verify Layout OK Cancel

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You will make just a few changes here to reflect the general goal of particle sizing. Change the *Last Delay* in the Delay Range section of the window to 10 ms. Deselect the *Low Speed Circuit* in the Circuits section of the window. The middle speed section can handle a last delay time of 16,384 times the first delay, or ~82 ms given a 5 μ s first delay. Change the number of *Channels* in the Extended Channels section of the window from 4 to 8, and change the *Multiplier* from 4 to 2. This has the effect of placing 8 channels extended beyond the main group of contiguous channels such that the 8th extended channel is at two times 10 ms or 20 ms.

Click on the command button labeled *Verify Layout* at the bottom of the screen. Verify that your choices have been implemented. Click on *OK* to return to the main window.

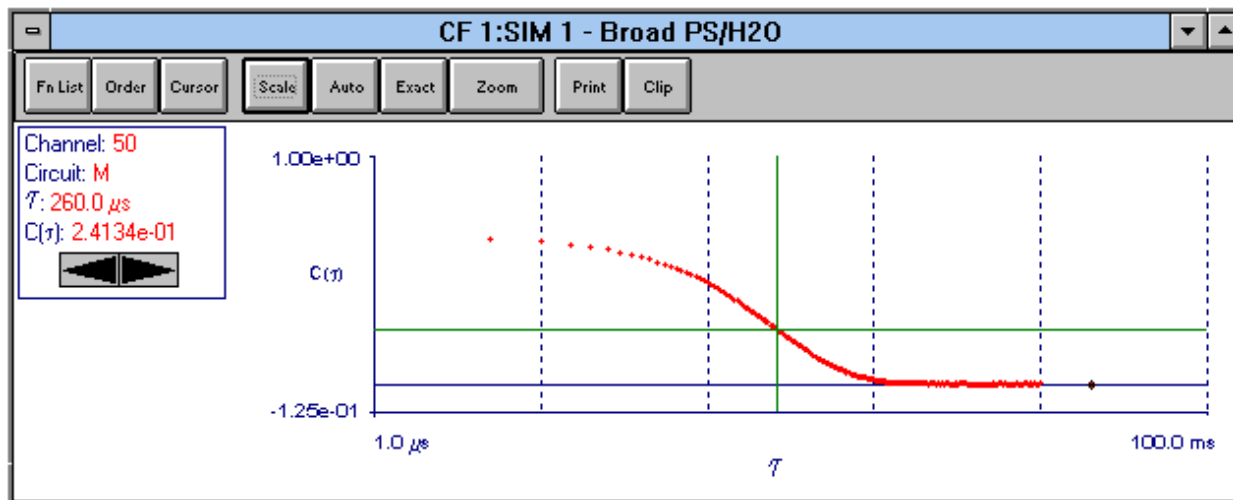
Prepare a Sample or Use the Simulator

Prepare a sample such as a 100 nm polystyrene latex in 10 mM NaNO₃. For the first measurement use a simple material, one that scatters strongly, is fairly narrowly distributed, and one for which you know the size reasonably well.

If you do not have a sample, you can still follow along by using the simulator. First, click on *Window* in the main window menubar. Click on *Close All*. Second, from the *Correlation Functions* menu select *Simulation Window* then *New Window*. Third, from the *Graphs* menu select *Correlation Function* then *New Graph Window*. Finally, from the *Windows* menu select *Smart Tile*. To emulate a single exponential, click on the *Signal* command button in the SIM control window. Then enter 250 kcps for Signal Rate, 0.65 for Signal Amplitude, and 0.02 for Noise Factor. Make sure the *Exponential Decay* button is marked, and enter 2,700, 1,800, and 1,350 rad/s for the first, second, and third Gammas, respectively. Click *OK*.

Make the Measurement

Now click on the green icon in the correlator control or simulator window. You should see the autocorrelation function (ACF) accumulate in the correlation function graph window.



Using the Cursor, Exact, and Auto Features

Click on the *Cursor* command button in the correlation function graph window. Move the cursor either by clicking on a channel in the graph or clicking on the left/right black arrows in the cursor control box. Information in this box includes the channel number, the correlator circuit (**Hi**, **Middle**, **Low**), the delay time, and the Y-Axis value, the magnitude of which depends on the display normalization.

Click on the *Exact* command button to scale the ACF over the entire Y-Axis scale. Click on the *Auto* command button to see the ACF accumulate as time passes.

Scaling the Autocorrelation Function Graph

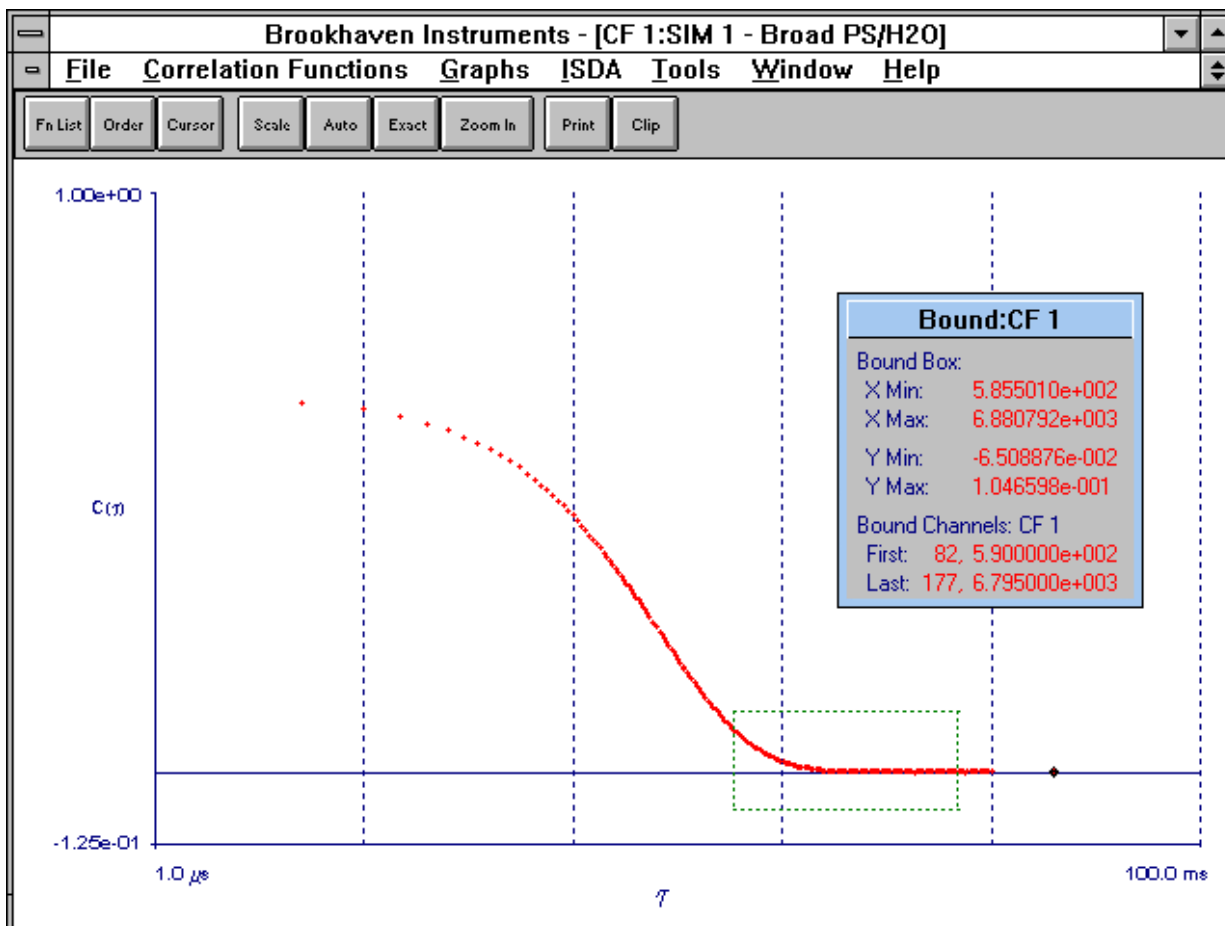
Click on the *Scale* command button. You can scale the X- and Y-axes independently, either logarithmically or linearly, or you can set a fixed scale with minimum and maximum values over which the function will be displayed. Try various combinations to see the effects.

For **display** purposes only, not affecting the calculations, you can choose one of three normalizations: raw, measured baseline, or calculated baseline. For **calculation** purposes, choose measured or calculated baseline from the menu obtained after clicking on the *Params* command button in the correlator control window.

Drawing a Bound Box

Click on the *Cursor* command button to close the cursor control window. You must close this window in order to enable the bound box feature. After closing the window, click anywhere on the graph and drag the mouse, creating a box over any group of channels. The dashed green box shows approximately the X and Y coordinates of the box, and the window that appears shows the exact limits of the box.

Notice that the command key labeled *Zoom* has now changed to *Zoom In*. Click it to see a magnified version of the ACF covering just the range of the bound box. This is useful for examining the shape of the ACF in the tails, at the beginning of the measurement, or to judge the noise. Notice the *Zoom In* button has changed again to *Zoom Out*. Click it to return to the previous view. You may zoom in successively to see more and more details.



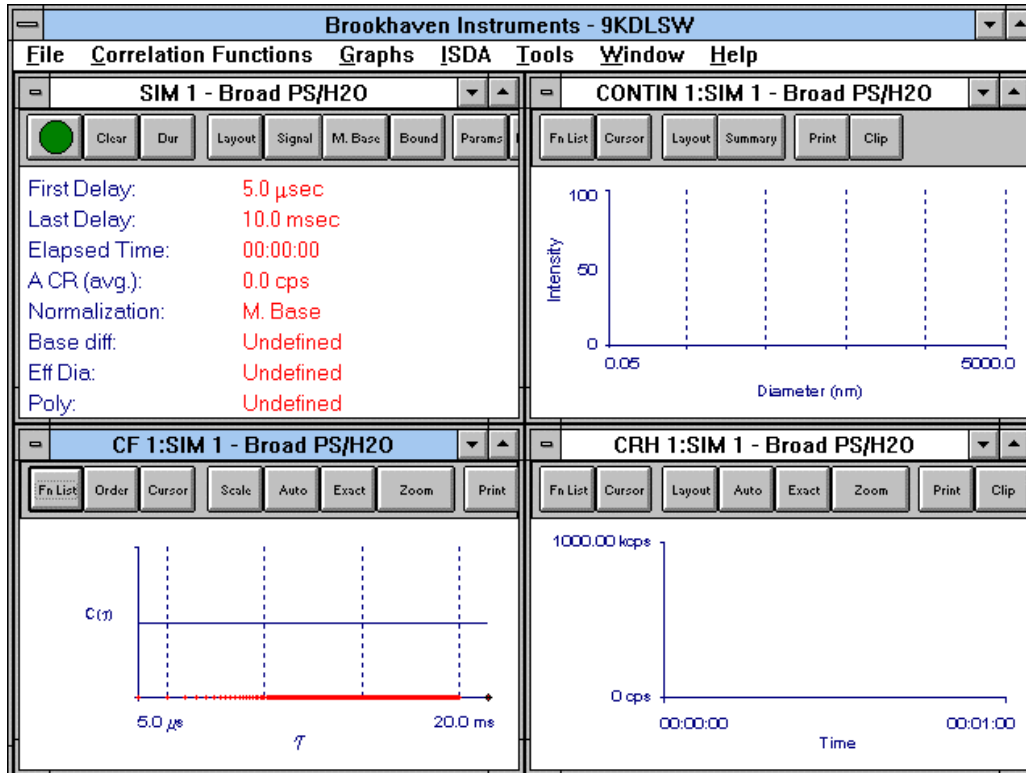
Changing the Display Window

You will now make changes to the correlator control window to display just the parameters you want to see. Click on the *Display* command button in the correlator control window. Notice the large list of possible parameters that can be displayed. The ones that are marked are currently displayed. Disable the following ones by clicking on them: Start/Stop, Samples, A_{tot} , Measured Baseline, Calculated Baseline. Enable the following ones by clicking on them: Effective Diameter, Polydispersity, Normalization. Click on *OK* to see the newly designed window.

Setting Up Multiple Windows and Using Smart Tile

Now there is more space in the main window. You will fill it with two more useful windows. Click on *Graphs* in the main window menubar. Click on *Count Rate History*. The new window that appears covers some of the other two windows. You could size it and drag it into a convenient position as you would any other window, but for now leave it alone. When the start button is pressed the intensity vs. time is plotted in this window from which sharp peaks corresponding to dust events can be seen and, if any exist, trends in the intensity, indicating a lack of stability.

If you purchased the optional BI-ISDA integrated size distribution analysis package of algorithms, click on *ISDA* in the main window menubar, and then click on *CONTIN* followed by *New Graph Window*. A fourth window appears making the screen look quite messy. Now click on *Windows* in the main window menubar and then on *Smart Tile*. Click on *Clear* in the correlator control or simulator window. Notice the four windows now look like the following:



If you did not purchase the BI-ISDA option, click on *Graphs* followed by *Lognormal Size Distribution*. Now follow the instructions above for creating four equal windows.

The Lognormal distribution is a two parameter fit obtained from the two parameters of a second order cumulant fit, the Eff. Dia. and Poly. These parameters and the cumulant technique, as well as the optional ISDA fits, including CONTIN, are explained in a separate section.

Starting Over

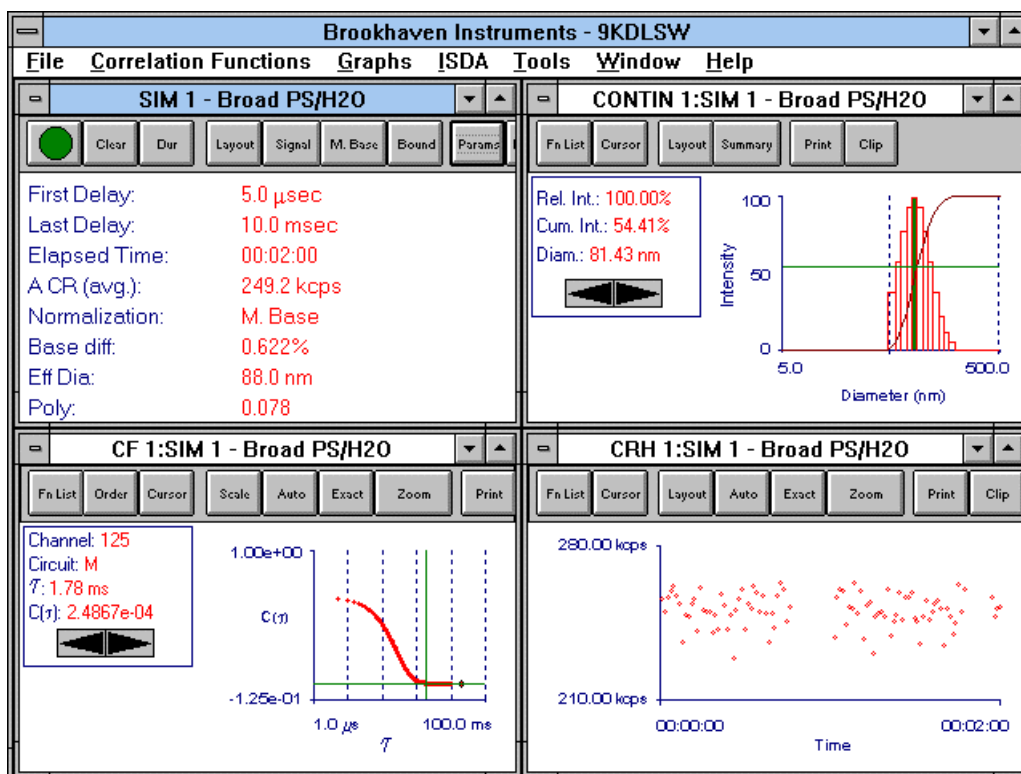
Click on the green, start icon in the correlator control or simulator window and watch the changes in each of the four windows. Notice that the CONTIN window does not show anything until 45 seconds have elapsed. This is normal and this update interval can be set from the *ISDA* menu. During the time calculations are made a small box at the current cursor position shows the letters "ISDA". While calculation are being made, no points are added to the count rate history. At the end of the calculation period the count rate history resumes with a gap in time equal to the calculation period.

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If you have a real sample, the count rate history may show many sharp peaks indicating you did a poor job of cleaning the liquid and/or sample cell. Perhaps the sample itself is full of dust and attention must be paid to cleaning it without distorting the actual size distribution of interest.

Notice the Effective Diameter and Poly in the control or simulator window. These two values are often all one needs to characterize the distribution.

The picture below shows the results after two minutes of simulation from a strongly scattering sample.

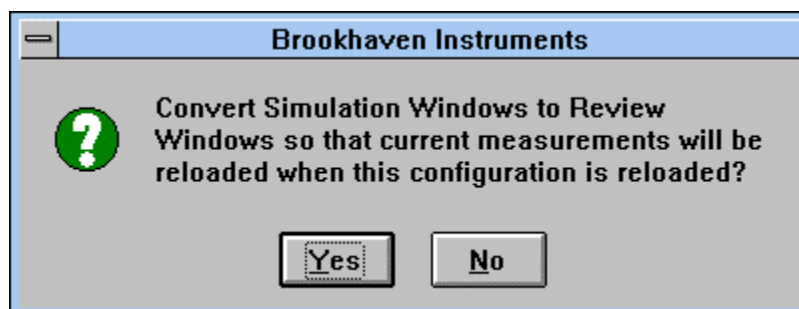


Saving Correlation Functions

To save the correlation function click Files. Then click *Save Correlation Function* (or use the hotkey combination Ctrl S). The data is automatically saved in whatever folder is opened in the database (*Files, Database*) and the Sample ID currently entered into the *Params* window is used. Alternatively, click *Save Correlation Function As* and you have the opportunity to select the folder and change the description/Sample ID. You may choose to *Export* the data file in which case a standard ASCII file format is created for use with the DOS BI-9000AT program or for use in plotting the correlation function in a spreadsheet or for use with user-supplied data analysis programs.

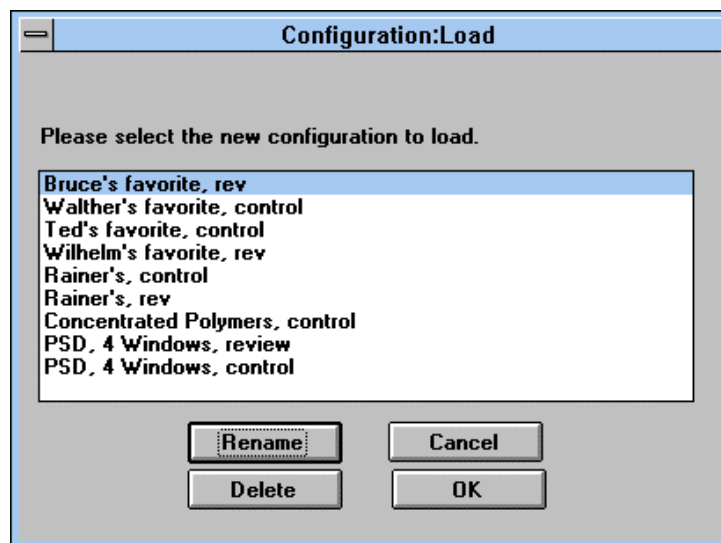
Saving Configurations

To save the current configuration, the 4-window configuration, for future use, click *Files, Save Configuration*. The following window appears:



You can save a configuration in two ways: as **review** windows with current data (click *Yes*); or as **control** windows without data (click *No*). You can save a configuration both ways by repeating the process after saving it one way. Saving it as a review window is very convenient for reloading previously saved correlation functions and having them reappear with all the chosen configuration's windows and calculations automatically implemented. Saving it without data as a control window is very convenient for reloading the configuration and using it to accumulate new functions.

To see what is currently saved as a configuration, click *Files, Load Configurations*. Here is an example of what you might see:

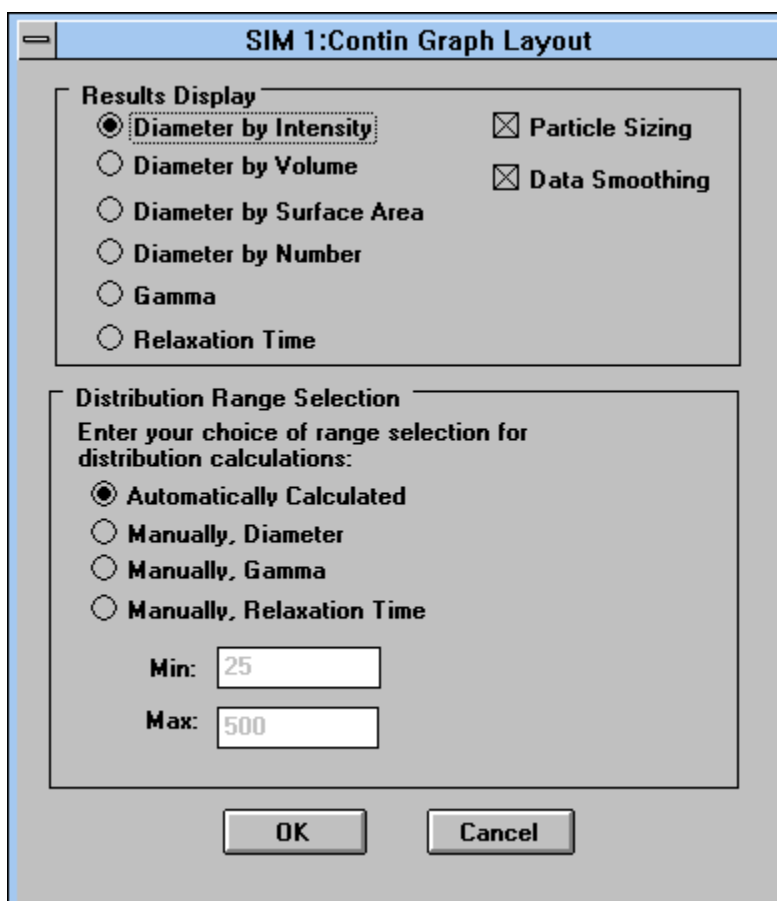


When you do save a new configuration, include in the name “review” or “control” or abbreviations to that effect so you may distinguish between the two types. Up to 25 configurations may be saved and loaded.

Notice the command buttons labeled *Layout* and *Summary* in the size distribution graph window, the one labeled CONTIN in this particular example.

Distribution Graph Layouts

Click on *Layout* and a window like the following appears.



In this window you can select the weighting, and therefore the display, of the distribution by: intensity, volume, surface area, or number. Surface area weighting assumes nonporous surfaces. Although number weighting is offered, a DLS machine is incapable of counting single particles and the weighting is only a mathematical transformation not usually acceptable when number distributions are required. Intensity weighting is closest to the raw data and is recommended.

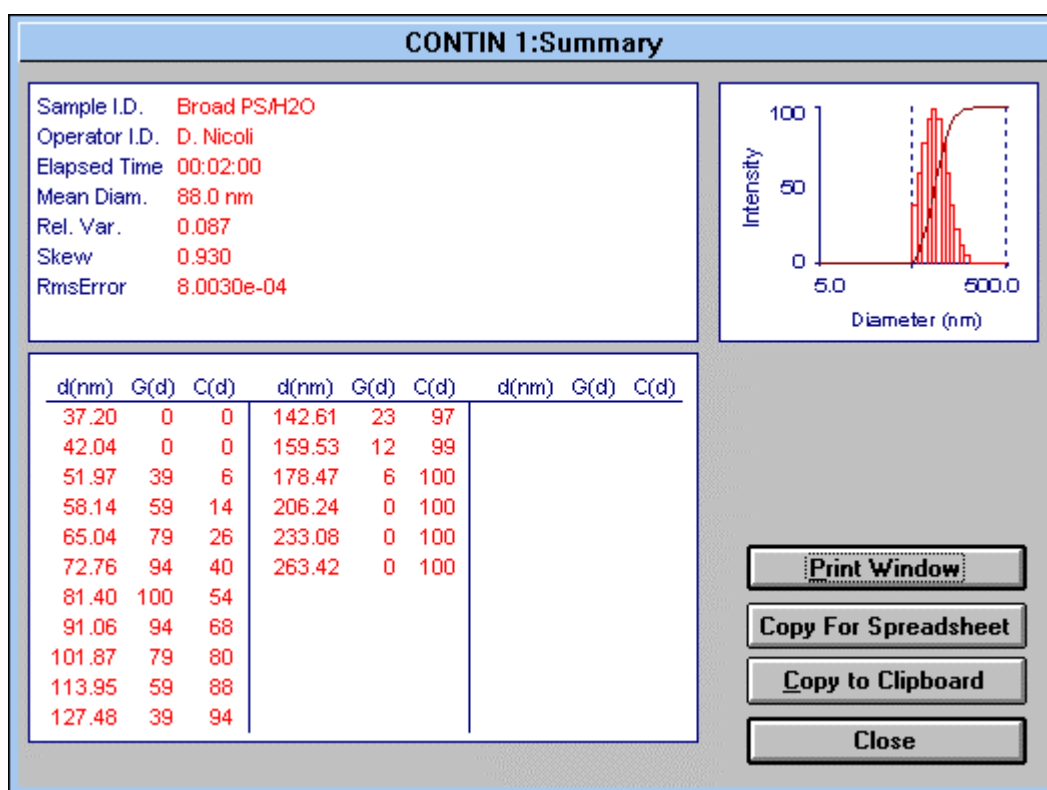
Data Smoothing normally yields symmetric peaks on a log scale while preserving the average and area under the peak obtained before smoothing.

For work with polymers, gels, glasses, and other complex fluids, the data can be displayed as intensity-weighted by linewidth (Gamma, Γ) or by relaxation time ($\tau_r = 1/\Gamma$).

For fitting you can either rely on the choices the program makes *Automatically* for maximum and minimum values, or you can supply *Manual* values by clicking on the appropriate buttons. When the range is *Automatically* selected for particle sizing, if the box labeled *Particle Sizing* is marked, then the range during all iterations is constrained between the limits of 1 nm and 10 μ , though the final answers will normally fall within a much more constricted range.

Distribution Summaries: Tables, Moments, Graph

By clicking on *Summary*, a command button in the distribution graph window, the following window appears.



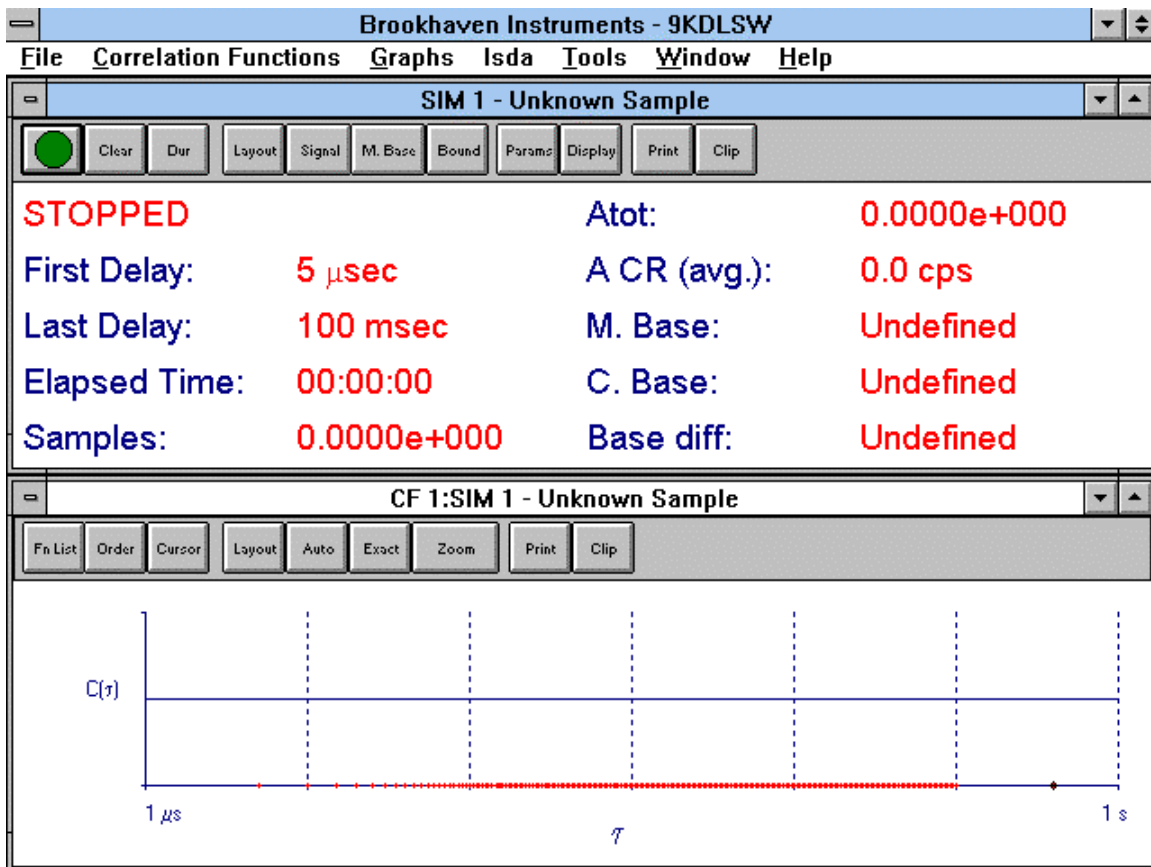
G(d) and C(d) are the histogram and cumulative values for the distribution by diameter d, weighted by whatever display was chosen (intensity, volume, surface area, number). From the d and G(d) values the mean, relative variance (variance \div mean squared), and skew (third moment about the mean \div variance^{3/2}) as well as the **Root-Mean-Square Error** are calculated. A small graph is also shown.

You are finished! With this quick tour of the most commonly used features of this program you should feel confident enough to motor around the program and discover what it has to offer. For more details, read the next several sections and the appendices.

Section VI: Screen Tour — Main Window Menubar

General Description

The simple look of the DOS version of correlator software is maintained as the default configuration. The delay time range, monitor channels, and baseline information are displayed in the top window; whereas, the bottom window shows a graph of the correlation function. Each window has a toolbar with command buttons activated by a single click. The following image shows the default configuration.



This default configuration can always be accessed by selecting *Restore Default Configuration* in the File menu. If you find the screen too cluttered, restore the default configuration and start over.

The File menu is the first choice in the main window menubar. The overall layout of the screen, the selection of signal source, the number and types of graphs, the optional ISDA fits, and the advanced tools (synchronization and scripting) can all be accessed from the main window menubar.

In the following paragraphs the most commonly used features obtained from the main window menubar will be explained.

File Menu

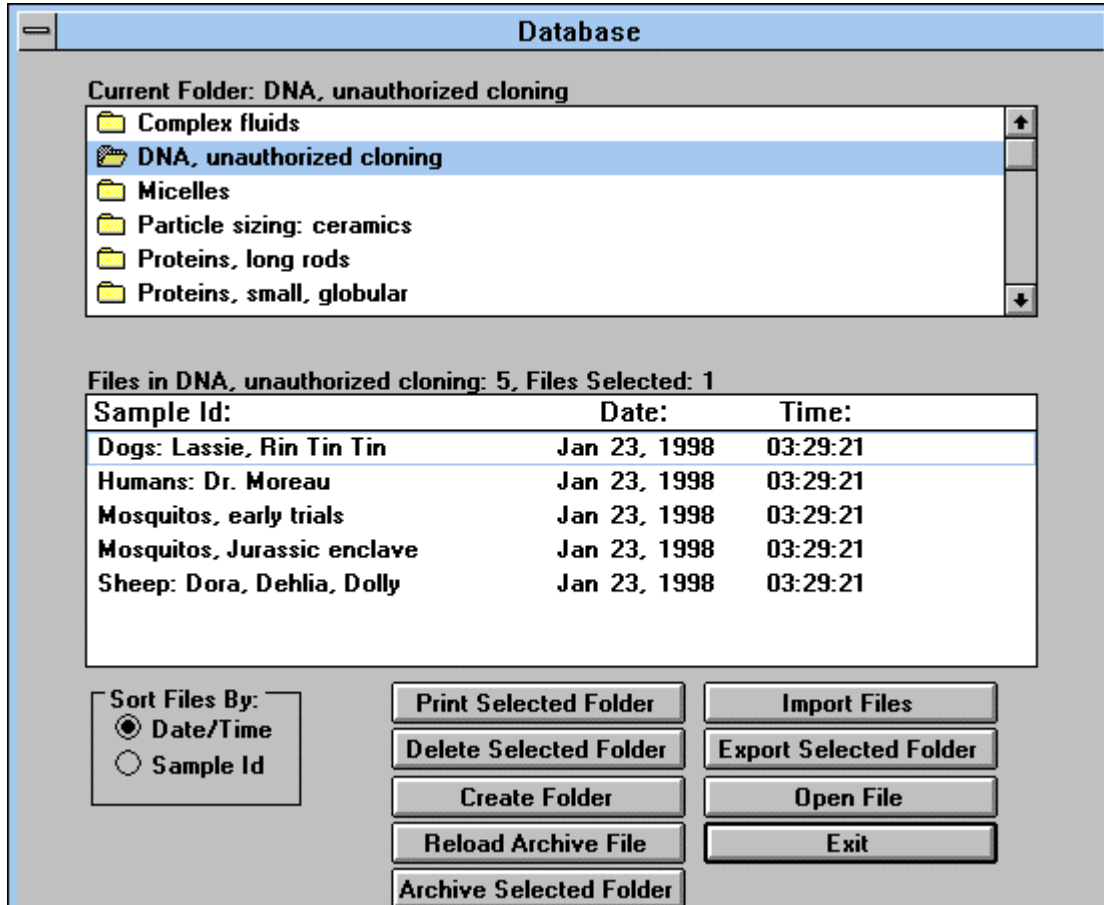
File	C orrelation Functions	G raphs	I SDA	T ools	W indows
Save Configuration					
Save Configuration As...					
Load Configuration					
Restore Default Configuration					
S ave Correlation Function				Ctrl+S	
Save Correlation Function As...					
D atabase					
Re u ild Database Index					
L og File Settings					
Reset Log File					
R eport File Settings					
Create Report File From Saved Measurements					
P rint Main Window				Ctrl+P	
Print Current Window					
Print Report					
Report Print Preview					
Report Print Options					
Print Setup...					
C lose All					
E xit					

A grouping of user-selected windows defines a configuration. Click on *Save Configuration*. Commonly used configurations can be saved by name and recalled. For different applications or different users, define the configuration that you want by opening windows, sizing them, and dragging them into position. Then save the configuration by name. The default configuration can be restored any time. You may save a configuration with data and later recall the configuration as a review configuration into which previously saved correlation functions may be loaded. This is useful for analyzing previously saved data with a new configuration. You may save a configuration without data and later recall the configuration from which new data may be accumulated. You may save a favorite configuration both ways, giving each a different name. We suggest including in the name the designation “Review” or “Control” to indicate which type of configuration it is. Up to 25 configurations may be saved/recalled by name.

Use Ctrl S to save accumulated correlation functions by name.

Click *Database* to access **folders/files** for recalling data files.

Database



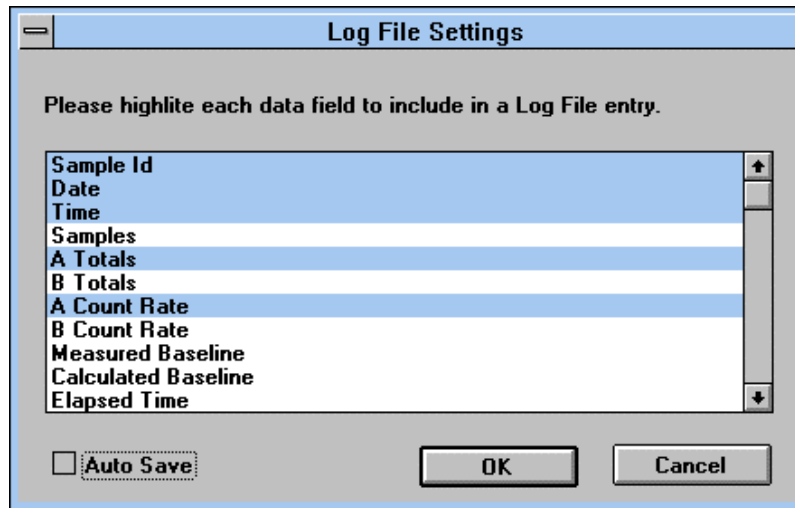
Results are saved in the currently opened **Folders** as **Files** using the Sample ID, Date, and Time as file identifiers. Click **Create Folder** to create a new one by name. Double click on a folder to open it and have access to the files. Single clicking on a folder selects, but does not open, the folder. Once selected the entire folder may be deleted, printed, or archived. Archived files are in binary format suitable for use only with the DLSW program.

Files can also be selected by clicking on them, opened, deleted, printed, and archived. Files can also be exported in an ASCII format suitable for use with other programs such as the DOS version of the correlator program or spreadsheets or user-supplied data analyses programs. To select a string of files, click on the first, then, holding the Shift key down, click on the last. To select nonconsecutive files, hold down the Control key while clicking on files.

You can name a maximum of 250 folders. The maximum number of files per folder is also 250. The total number of allowed files in all folders is limited to 50,000. But don't you think if you reach any of these limits that you are spending too much time in the lab?

Screen Tour —Main Menus: Page VI-4

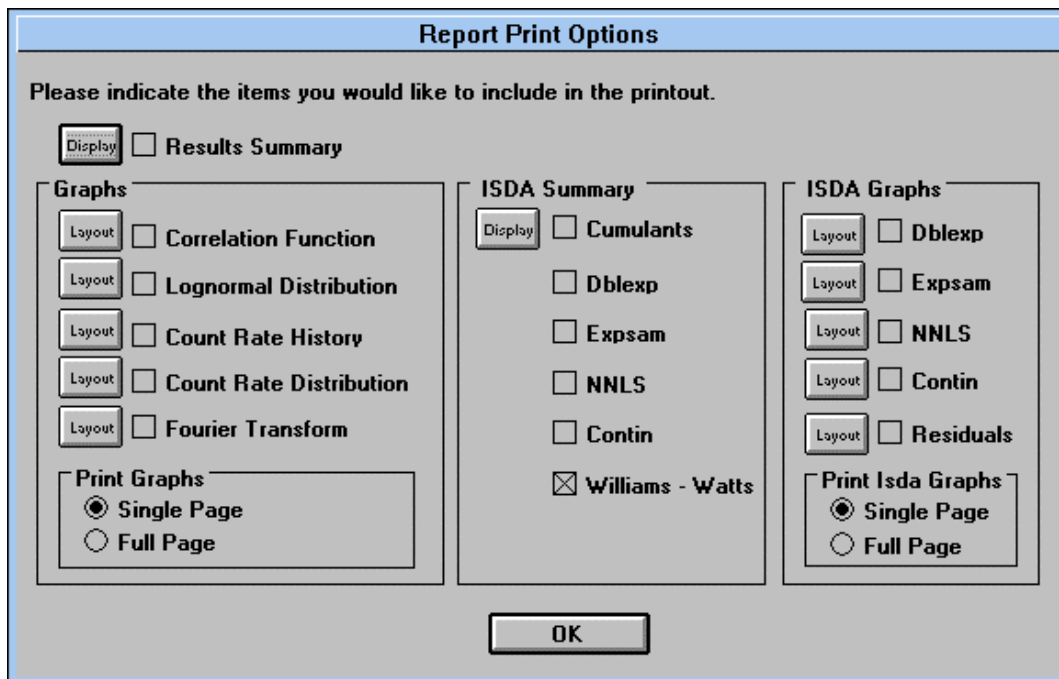
To create a single data file from multiple measurements, with a subset of just the values you want, click *Log File Settings*. Here you can select a subset of measured values and input parameters common to all data files for inclusion in the log file. The log file is ideal for use with spreadsheets.



To initiate the automatic logging of the selected values, click the *Auto Save* box.

To create a log file from previously saved files, click *Create Report File From Saved Measurements*.

Report Print Options



Click *Report Print Options* to design the printout; click *Report Print Preview* to see the output on screen before printing; and click *Print Report* to initiate the printing.

Within the *Report Print Options* window you can decide what will and will not be printed; whether graphs will be printed altogether on a single page or whether they will be printed on separate pages; and you can change the layouts of printed material such that it will be different from the appearance on the screen. It is your choice.

Click *Print Setup* to select the printer and control its capabilities. If your printer or computer is memory limited, select draft quality output instead of proof quality. In most cases, draft quality provides the fastest outputs with adequate print quality.

Correlation Functions Menu

<u>C</u>orrelation Functions	<u>G</u>raphs	<u>I</u>st
Correlator Control Window		▶
Correlator Simulation Window		▶
Aux. Display Window		▶
File Review Window		▶

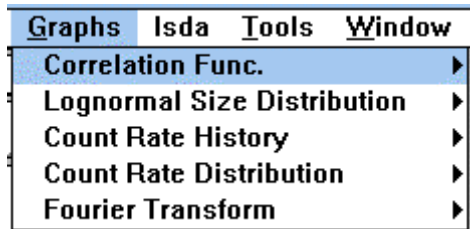
Click *Correlator Control Window* to establish a link between a signal source (typically the A input) and the program. An example of a correlator control window is the top window in the default configuration. The correlator is controlled from the command buttons in the toolbar of the correlator control window: Start/Stop, Clear, Channel Layout, Experiment Duration, etc.

Click *Correlator Simulation Window* as the first step in creating a simulation of a correlation function. Simulations are useful in learning the program without a real signal source and for creating model results which can be overlaid on actual data.

Click *Auxiliary Display Window* to isolate just one or two of the parameters in a control window. For example, when aligning the BI-200SM, it is convenient to have a very large display of just the count rate so that adjustments made on the goniometer can be conveniently related to changes in the intensity visible in the enlarged, auxiliary window, even from across the room. Or, put the effective diameter in an enlarged window and watch it update from across the room as more data is accumulated.

The File Review Window is used in two different ways. This window is automatically created when you recall data by clicking on a particular file, in an open folder, accessed from the File, Database menus. You can also open a File Review Window from the Correlation Functions Menu. The data will then be a static image of the currently selected correlator control window information. In this way you can take a snapshot of the earlier correlation function, even overlaying it with the currently accumulated function. You can open several File Review Windows at the same time.

Graphs Menu



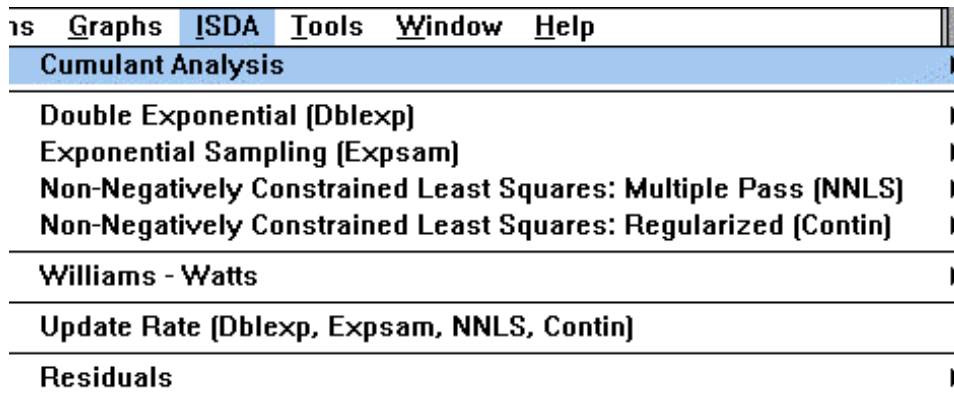
Click *Correlation Function* to display a graph of the correlation function. This is demonstrated in the bottom half of the default configuration. The toolbar allows you to manipulate the layout of the graph and to zoom in/out on portions selected by dragging a box over sections of the correlation function. The Function List allows you to turn on/off up to 6 currently available functions for the purpose of comparing the shapes.

Click *Lognormal Size Distribution* if you want a two-parameter fit to the particle size distribution obtained from the first and second cumulants of the intensity weighted diffusion coefficient distribution.

The Count Rate History and Distribution windows are helpful in judging the stability of the scattered signal, identifying any “dust” events, and spotting any systematic trends that may signal a laser that is not stable or other sources of instability in the system.

The Fourier Transform window is only used with linearly spaced data, and will yield the power spectral density function in frequency space of the scattered laser light.

ISDA Menu



The BI-ISDA is an **option** that allows the correlation function to be analyzed for particle size distribution information in a variety of ways. The operator can select weighting by scattered intensity, particle volume, surface area, or number. Data can be analyzed in Γ or τ space as well. This may be useful for polymer solutions, gels, glass transitions, and

other complex fluid measurements. A Williams-Watts fitting function is also available. If you do not see this menu item on the main window menubar, or if it is greyed out and not accessible, you have not purchased this **option**. In this case, please go to the next section

Click *Cumulant Analysis* to open up a window with four individual fits to the correlation function: linear, quadratic, cubic, and quartic.

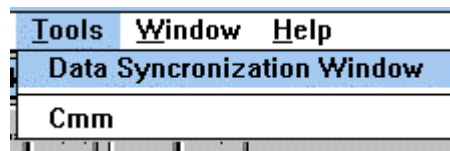
The cumulant analysis yields only moments of the distribution. For more information, select one of the other fits. These fits are described in more detail in a different section of this manual.

The cumulant results and the other ISDA fits are updated at the rate you select in the *Update Rate* window, and each is displayed in its own window. You may find, depending on the speed of your computer, that the update rate is not suitable. In this case, click *Update Rate* and change the interval in seconds between updates. Shorter intervals may suffer from, initially, noisy data. In addition, the *Count Rate History*, if it has been enabled, will contain gaps during the fitting period. To reduce the gaps, increase the update interval.

Click *Residuals* to open a window for viewing the difference between the fitted and measured correlation functions. You may also compare the residuals from any two fits. The residual plots are updated periodically, and the periodicity can be controlled from the *Update Rate* window discussed previously.

Residuals can be displayed even if the function chosen for the fit is not.

Tools Menu



This menu covers two special cases.

The first case involves multiple correlation functions. You may have two signals, one in input A and the other in input C, or one in Input A and the other simulated, and you wish to autocorrelate both. Or you may have multiple correlator boards with one or two inputs per board. Each input would have its own Correlator Control window, and each may have its own Correlation Function graph window. When you want to Start/Stop/Clear all the functions simultaneously, click *Data Synchronization Window*.

For automatic data collection, click Cmm. This feature consists of an advanced scripting language that allows complete control of the correlator. Scripts are written,

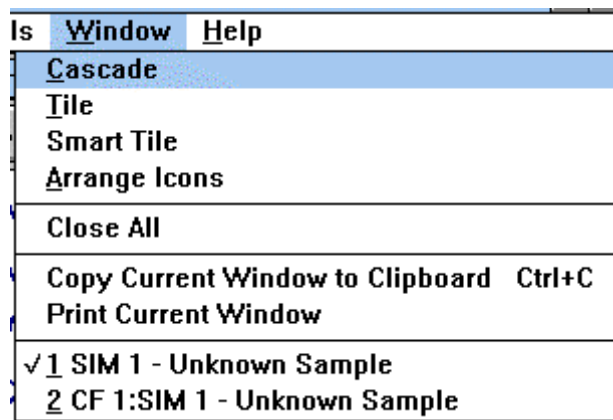
saved/reloaded, and implemented by a single mouse click. See the appendices for more details.

Motor Menu

There are two choices under this menu: Set Angle and Release Motor Tension.

Click *Set Angle* to set the current angle and to set the destination angle. Click *Release Motor Tension* when you want to decouple the motor controller from the motor. Do this when you are aligning the system.

Window Menu



There is nothing new here that you have not seen in most windows-based programs with one exception: Smart Tile. If you find several windows open simultaneously, positioned and sized inconveniently, click *Smart Tile*. The resulting arrangement is symmetric, and, while perhaps not your ultimate goal, is a good place from which to start a customized configuration.

REMEMBER: If you have taken the effort to arrange several windows, *click Save Configuration* in the File menu, and give the configuration a name. This will save you time when you want to reload the same configuration.

Help




The most important information here is the version number, 1.35 in this particular case. When contacting the factory, please make note of the version number. Some problems may be solved by simply updating to a more recent version.

If you are a registered customer of Brookhaven, updates can be sent using ftp. Contact us by email at tech@bic.com for instructions on accessing our server to implement the electronic transfer. Some people “borrow” our programs, and they are not officially entitled to updates. If you would like the latest software anyway, please contact us and we can discuss your flagrant violation of international copyright laws.

Section VII: Screen Tour – Correlator Control Window

General Description

To manipulate the correlator control window shown below, the command buttons in the toolbar are used. In this section of the manual the various features available in this toolbar are described. To follow the discussion, it is best to have the program running. The obvious features like Print and Clip (to clipboard) require no further discussion.

	Clear	Dur	Layout	Signal	M. Base	Bound	Params	Display	Print	Clip
First Delay:	5.0 μ sec	Liquid:	Aqueous							
Last Delay:	100.0 msec	A CR (avg.):	249.9 kcps							
Elapsed Time:	00:02:00	Normalization:	M. Base							
Wavelength:	632.8 nm	C. Base:	3.7208e+07							
Angle:	90.0	Base diff:	0.104%							
Temp:	25.0 deg C	Eff Dia:	95.2 nm							

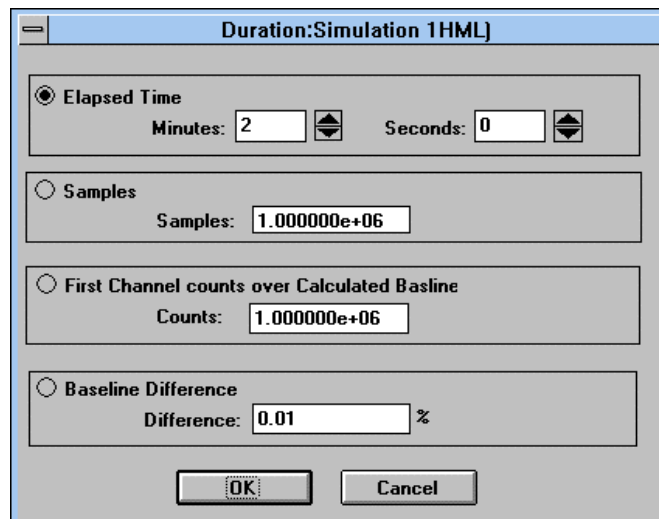
Start/Green and Stop/Red Icon

Click the *Green/Start* icon to start or the *Red/Stop* icon to stop the accumulation of the function. Otherwise the function will stop accumulating when the duration set has been reached. See below for a description of the various ways to set duration.

Clear

Click the *Clear* button to delete data from memory. You may do this when the accumulation has stopped or during the accumulation. If you clear during the accumulation, the data collection starts over automatically.

Duration (Dur)



Duration:Simulation 1HML

Elapsed Time
Minutes: 2 Seconds: 0

Samples
Samples: 1.000000e+06

First Channel counts over Calculated Baseline
Counts: 1.000000e+06

Baseline Difference
Difference: 0.01 %

OK Cancel

The duration of the experiment can be set in four ways.

1. As total *elapsed time* in minutes and seconds. Note: the actual accumulation time is approximately the value set, due to the overhead involved with controlling the hardware.
2. As total *samples*, in which case the experiment duration is the number of samples times the sampling time of the middle speed circuit (or low speed if that is the only circuit enabled.).
3. As the *difference* in the *channel contents* between the first delay channel and the infinite time delay, also known as the calculated baseline, since this value is calculated not directly measured.
4. As a percent *difference* between the measured *baseline* (bound box, autoslope, or extended) and the calculated baseline.

Layout

Correlator Setup Parameters: Simulation 1

Layout Requests

Channel Spacing

Linear

Linear with offset

Ratio

Delay File [v]

Channels Requested:

Extended Channels

Channels: Multiplier:

Delay Range (micro seconds)

First Delay: [v]

Last Delay:

Signal Source

Auto A Auto C Test

Cross A/B Cross C/D

Circuits

Digital Input

Use Hi Speed Circuit

Use Mid Speed Circuit

Use Low Speed Circuit

Wait for valid history

Analog Input

Layout Results

First Delay:	500.0 nsec	Channels Mid:	16
Last Delay:	100.0 msec	Sampling Time Mid:	500.0 nsec
Channels:	38	Channels Low:	22
Extended Channels:	4	Sampling Time Low:	50.0 μ sec
Extended Last Delay:	400.0 msec		

The layout of the correlation function is determined by settings in this window. The window is divided into sections, and these will now be described.

Channel Spacing

Linear spacing occurs when the delay times are equal to the sampling times. Linear spacing can only be selected with either the middle speed or the low speed circuits enabled, but not both. [See the *Circuits* section description below.]

If you choose linear spacing, the last delay time you selected is ignored. Instead, the last delay is determined by multiplying the first delay by the number of channels requested. For example, choosing a first delay of 10 μ s and 100 channels, yields 100 channels spaced at 10 μ s and a last delay time of exactly 1 ms. Note: If the total delay time range exceeds the limits of the circuit, then the number of channels may be less than the requested number. See the section entitled Theory of Operation.

If you choose *Linear with offset* spacing the user chooses the first and last delay times and specifies a number of requested channels. The program attempts to fulfill the request with linear spacing. However, due to hardware limitations, the channel spacing may be close to, but not exactly equal to, linear spacing. For example, choosing a first delay of 10 μ s and a last delay of 1 s, with 100 channels, will result in spacing of approximately 11.11 ms. The slight offset from exact linear spacing results from the user request for the first *and* last delay as well as the number of channels and the hardware limitations.

Ratio spacing is the most common, and allows the greatest flexibility. As explained in the Theory of Operation section, a constant ratio between successive channels is approached, provided there are at least a few decades of total delay time. Initially, the channels are spaced linearly in the first delay time of the middle speed circuit.

Delay file spacing allows the user to recall a previously stored file name with the extension .dly. Such a file determines not only the spacing but also the number of channels, the first and last channels, and the baseline channels.

Three examples of delay files are provided as standard. The first two are appropriate for diffusing wave spectroscopy, covering the range from 25 ns (requires the high speed circuit option, BI-25NS). The third delay file is an example showing the use of all three circuits, high, middle, and low.

To write your own delay file use an ASCII text editor such as Window's Notepad. Recall one of the standard files provided such as c:\bicw\dlyfil\128_2us.dly. Modify it for your own use. Save it as a new file with a name. Make sure to add the extension .dly and to store this new file in the same path (C:\BICW\DLYFIL) so the application program will find it. Delay files are described in more detail in the appendices.

Delay Range

From the list box select the first delay. The values displayed depend on which circuits you have enabled (see *Circuits* section below) and whether or not you have the 25 ns option.

Choose the last delay by entering a number in microseconds. Scientific notation makes this easier.

It is suggested that you choose, for particle sizing, a last delay such that the ACF has decayed to what look like a flat line over approximately a decade in delay time when the display of the function is not in the zoom mode. It is further suggested that, when the delay time axis is displayed logarithmically, the first delay time is such that the ACF looks again like a horizontal line.

Signal Source

Select the signal source. Most often you will be autocorrelating the signal from Input A.

Channels

Enter the number of channels you would like. The maximum allowed is 522, if you purchased the optional 12, 25 ns channels. Otherwise, it is 510. However, given the requirement that the correlator will operate in real-time and as close to 100% efficiency as possible, the actual number may be, in some cases, less than the number you request. [See *Verify Layout* below.]

Extended Channels

Enter up to 8 channels. Enter 0 if you don't want any extended channels. The average of the number you select, if Extended Channels are subsequently chosen for normalization, will become the Measured Baseline.

Select a Multiplier up to 10. The number 2 is the minimum. The multiplier determines the value in delay time of the last of the extended channels. For example, if the first delay is 5 μ s and the last delay time is 10 ms, and the number of extended channels is 6 with a multiplier of 4, then the last of the 6 extended channels occurs at a delay time of 40 ms. The spacing between extended channels is linear.

Circuits

Click on the appropriate box to enable or disable circuits. For particle sizing select just the Middle Speed Circuit. Add the Low Speed Circuit for delay times, including Extended Channels, greater than 1.6384 seconds, and for delay time ranges covering more than 16,384 times the first delay time chosen with the Middle Speed Circuit. [See the Theory of Operation section for more detail.]

If you do not have the optional 25 ns channels, the High Speed Circuit starts at 100 ns. If you do have the High Speed Circuit option, then its first delay channels starts at 25 ns. The first delay of the Middle Speed Circuit starts at 500 ns and that of the Low Speed Circuit starts at 50 μ s.

Wait for Valid History

This selection is not required to make valid measurements, but is included for aesthetic reasons only. By definition, it is impossible to display a particular delay time until that amount of time has passed since clicking the start icon. For example, if the last delay time is 100 seconds, and the *Wait for Valid History* is checked, then points on the correlation function graph window will be added as the time increases. After 100 seconds the last point is added and the ACF continues to accumulate until the duration is reached.

Some people find this display confusing and prefer not to wait until the last delay time has passed before all data for all delay values is displayed. To accomplish this, deselect the *Wait for Valid History* feature.

Digital/Analog Input

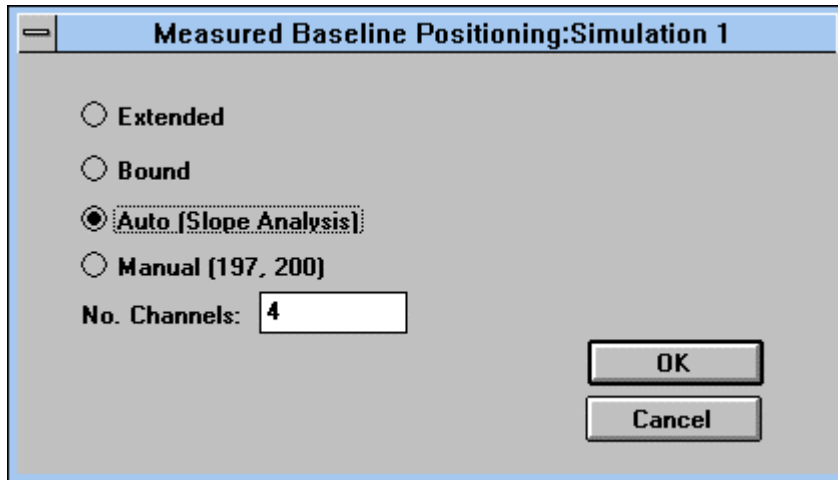
With few exceptions, choose Digital Input and then enable one or more of the three circuits as discussed above. Since April of 1997 the BI-ANIN analog input option has been available. This requires a signal input ranging from $- 2.5$ to $+ 2.5$ VDC. The analog input option has some use in scattering from liquid surfaces. Contact the factory if you have another application.

Verify Layout Command Button

Click the *Verify Layout* button to view what the actual number of channels will be and to view what the sampling times will be. If you have selected a large number of channels, and a small delay time range, the number of actual channels enabled will be less than you requested. The same is true if you selected a low first delay time, a large number of channels, and linear spacing. You get the most linearly spaced channels in the middle speed section when the first delay time is 5 μ s or higher.

You may also bypass the Verify Layout and go directly back to the correlator control window by clicking on OK.

M. Base



You can select 3 different types of measured baselines: extended, bound, or autoslope. Click *M. Base* in the correlator control toolbar. Click *Extended* to select the 1 to 8 extended channels as chosen in the *Layout* section of the correlator control window.

In the M. Base window, click *Bound* to select up to 32 channels, *anywhere* in the function, that have been previously bound.

*NOTE: After creating the bound box as explained below, **do not** click the Bound command button in the toolbar. Click the Bound button in the M. Base window. If you click the Bound command button in the toolbar, you will reset the delay time range to the bounded region. See the discussion in the next section entitled "Bound".*

To bind channels click in the correlation function graph window of interest. Holding the left mouse button down, drag the mouse over a group of channels. A popup window appears showing you the minimum and maximum delay values (x axis values), the minimum and maximum ACF values (y axis values), and the first and last channel information (channel numbers and corresponding delay times in microseconds). You can create a bound box that covers much more than 32 channels, but only the *first* 32 will be used for the bound, measured baseline.

[NOTE: Creating a bound box using the mouse has two other uses: to set the scale for zooming In/Out, a useful tool for viewing dynamically the shape of the ACF in any portion of the curve; **and**, to reset the delay time range for the next run. These features are described elsewhere in more detail.]

To enable the automatic selection of a baseline, click *Autoslope* in the M.Base window. Starting half way down the function, every eight consecutive channels are fit to a straight line until the fitted slope is less than -0.07% times the amplitude of the first calculation channel. This procedure locates the first autoslope channel. From 1 to 32 channels,

starting from the first autoslope channel, are averaged to determine a measured baseline. The number averaged depends on the last number bound or set in the M.Base window.

Autoslope is useful when a few large particles distort the ACF. However, the autoslope feature can be counterproductive in the case of an ACF with a short, flat region between one fast and one slowly decaying region, both of which are of interest.

The Manual entry is not selectable. It indicates where the baseline has been placed in a fixed position by a previous “bound channel” placement.

Bound

You can quickly and conveniently reset the delay time range by dragging a box around the delay time range of interest in the correlation function graph window. Then click the *Bound* command button in the correlator control window. Notice that the first and last delay times change and that the graph changes to correspond to the newly selected range.

Note: Because the box you create may fall between channels, the actual range obtained will be within one channel on either side of the box as created. The first delay will be placed no higher than 40 ms when using the low speed circuit and no higher than 100 μ s if the low speed circuit is not used.

Params

Calculation Parameters: Ctrl BD 1 (HML)

Sample ID: Model Polymer Measurement

Operator ID: Raoul Flory-Huggins

Notes: Lattice Model

Temp.: 35.0 deg. C

Liquid: Cyclohexane

Viscosity: 0.761 cP

Ref. Index: 1.420

Angle: 90.00

Wavelength: 532.0 nm

Homodyne Self-Beating

Refractive Index of Particles:
 Real: 1.430
 Imaginary: 0.000

Normalization:
 Calculated Baseline
 Measured Baseline

First Calc. Channel: 2

Use Dust Filter

Dust Cutoff: 50.00

OK Cancel

Click on the Parameters command button to set parameters and to add identifiers to the run. The fields for several of the parameters are obvious and will not be discussed.

Sample ID

The value in the Sample ID field is used in the title bar of the correlator control window and as an identifier in the database. (See *Database* under File in the main menu.) So take some care in selecting an appropriate name.

Suspension

Several pure liquids are available as standard in the list box: aqueous, ethanol, methanol, benzene, toluene, hexane, cyclohexane, and heptane. If your liquid is one of these, select it. The viscosity and refractive index are automatically calculated, with corrections for the temperature and wavelength. Click *Unspecified* and type in the name of any other liquid. In this case you will have to specify the viscosity and refractive index at the temperature of the sample. Others liquids may be added to the list box upon request to the factory.

Refractive Index of Particles

The values input are only used in the conversion of the intensity-weighted distribution to the volume- and number-weighted distributions. The refractive index of the particle does not affect the cumulant (Eff. Dia. and Poly) or other intensity-weighted results.

Normalization

Select either Calculated or Measured Baseline. The Measured Baseline will be the average of either the extended channels, the bound channels, or the autoslope channels, whichever was selected in the *M.Base* window.

The baseline selected in this window **affects** the calculated results. The baseline selected using the *Scale* command button in the correlator graph window only affects the display of the data, **not** the calculated results.

NOTE: Measured baselines are always highlighted as thicker, blacker points in the function *even if they are not selected for normalization*. They are highlighted so the user will know where they occur in the function

First Calculated Channel

The number input is the first channel used in any fit to the ACF. This allows one to ignore short delay times that may be distorted due to afterpulsing. All PMTs suffer from afterpulsing to some extent, some more than others; and amplifier/discriminators may contribute ringing. Thus, it is useful to ignore accumulated channels that are distorted. Test for distortion using a pure liquid that scatters strongly like toluene.

Homodyne/Self Beat

In all experiments except a special few, the scattered light will beat against itself, producing decays in the ACF that vary like $\exp[-2\Gamma\tau]$. This is called self-beating. In this most common case click the box labeled Self-Beating.

In many parts of the literature, however, this is referred to, erroneously, as the homodyne mode. True homodyning occurs when two signals beat against each other, each derived from the same source.

Click the Homodyne box if the scattered light beats against a local oscillator, producing decays in the ACF that are proportional to sums over functions like $\exp[-\Gamma\tau]$. In many parts of the literature, however, this is referred to, erroneously, as the heterodyne mode. True heterodyning occurs when two frequencies beat against each other, each derived from different sources.

In DLS experiments there is usually only one source, so true heterodyning is rare. Furthermore, a local oscillator is normally derived from the same source—from a part of the main beam using a separate optical path or from flare light derived intentionally or unintentionally. This is true homodyning.

If you click in the Homodyne box, the Eff. Dia. will be approximately half of the value with this box empty.

Use Dust Filter

Click in this box if you wish to set the Dust Filter Cutoff number. A batch of data is rejected if its intensity is higher than the average of the previous five batches plus the standard deviation of the five times the number entered in the Dust Cutoff box. In this way, a sequence of data distorted by a burst of intensity due to residual dust may be trapped and ignored.

However, if the number is set too low, then natural fluctuations in intensity, which are the essence of DLS, may be erroneously discarded, and the final results inaccurate. It is always better to clean liquids and samples, either by filtration or centrifugation, than to rely solely on hardware and software. However, with a little experimentation for a particular sample, you may find a compromise that saves sample preparation time and still yields acceptable results. We have found that values between 25 and 50, for water-based samples, works reasonably well.

Display

Display Options

Please indicate the items you wish to display

Status <input type="checkbox"/> Start/Stop <input type="checkbox"/> Signal Source <input type="checkbox"/> Run Number <input checked="" type="checkbox"/> Delay Range <input checked="" type="checkbox"/> Duration	Correlator Data <input type="checkbox"/> Samples <input checked="" type="checkbox"/> A Totals <input checked="" type="checkbox"/> A Count Rate <input type="checkbox"/> B Totals <input type="checkbox"/> B Count Rate <input type="checkbox"/> Mid Speed Zero Chan.	Cumulants <input checked="" type="checkbox"/> Effective Diameter <input checked="" type="checkbox"/> Poly
Calc. Params. <input type="checkbox"/> Wavelength <input checked="" type="checkbox"/> Angle <input checked="" type="checkbox"/> Temperature <input checked="" type="checkbox"/> Liquid <input type="checkbox"/> Viscosity <input type="checkbox"/> Refractive Index	Baseline <input checked="" type="checkbox"/> Measured Baseline <input type="checkbox"/> Calculated Baseline <input checked="" type="checkbox"/> Baseline % Difference <input checked="" type="checkbox"/> Normalization	Dust Cutoff <input type="checkbox"/> Dust Cutoff <input type="checkbox"/> Data Retention Rate

OK Cancel

You can custom design the data shown in the correlator control window. By clicking on the appropriate boxes, you can turn on or off the display of:

- status information (run number, delay range, duration, etc.)
- monitor channel values (samples, count rate, etc.)
- cumulant results (Eff. Dia. and Poly calculated from a second order fit only)
- dust cutoff value and data retention rate (low rate suggests sample is bad)
- calculation parameters (wavelength, angle, etc.)
- baseline information (measured, calculated, percent difference, and which is used for normalization)

Simulations

The correlator includes a simulation feature. It is useful for learning the features of the correlator and creating perfect sets of data that can then be compared to real data.

To create a simulation, click on Correlation Functions in the main menubar. Click on *Correlator Simulation Window*. Notice that the toolbar now has a new command button, *Signal*. Click on *Signal*.

Signal Strength

Enter the count rate in kilocounts/second (kcps). The maximum for the simulator is 1,000 kcps or 1 Mcps. The correlator hardware can accept up to 40 Mcps.

Enter the **signal amplitude**, a number from 0 to 1.00. This is the amplitude *above* the baseline (baseline here defined as 1). A perfect DLS optical setup would yield an intercept/baseline ratio of 2.00. While such a perfect value has been approached using single mode fiber optics, most pinhole/lens detector optics yield values between 1.2 (not very good) to 1.7 (very good).

Enter a value between 0 to 1 to simulate equal, random **noise** on all the correlator channels. Zero represents no noise except that from computer roundoff error. Typical noise is represented by the value 0.02. Values above 0.10 represent very noisy signals.

Signal Description

You can simulate either exponential decays or a Williams-Watts function.

If you choose to simulate exponential decays, you may enter up to three functions each characterized by a decay rate, Γ , in rad/s (1800 rad/s is the equivalent of a 95 nm particle diameter, water, 25 °C, 90° scattering angle, HeNe laser) and a pre-exponential factor $G(\Gamma)$. The decay rate characterizes the decay in the first order, or electric field, autocorrelation function. And $G(\Gamma)$ is proportional to the electric field amplitude contributed by that component.

NOTE: With earlier versions of the program, the pre-exponential factors were always equal, signifying equal weight by intensity, and they were not visible as shown in the picture above. In later versions of the software, you can vary the pre-exponential factors from zero to one. To check if this feature is available, but not turned on, do the following. Using an ASCII editor such as NotePad, open the file `c:\windows\9kdlsw.ini`. In the first section, the one marked [General] find or add the line:

`ShowGGammaOnSimulation=TRUE.`

The electric field autocorrelation function of a Williams-Watts function is given by:

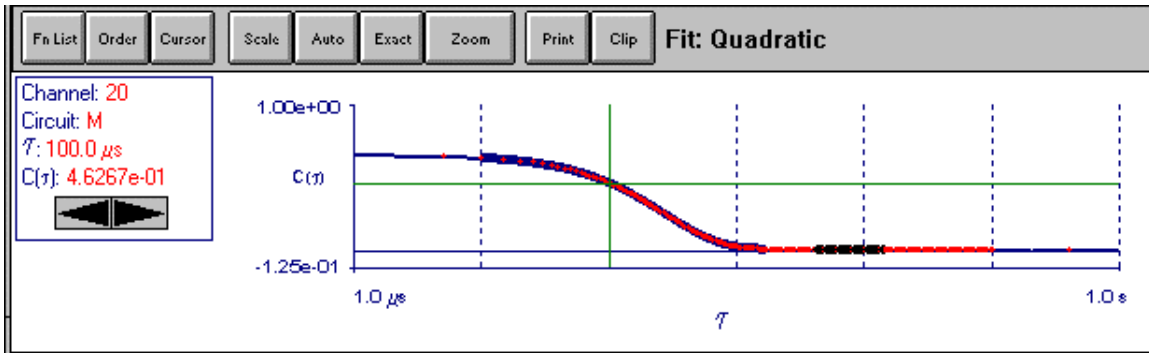
$$g^{(1)} = \exp \left[- \left(\frac{\tau}{\tau_r} \right)^\beta \right]$$

where the relaxation time is inversely proportional to the decay rate, $\tau_r = 1/\Gamma$. Here Γ is entered by the user as the First Gamma, just as if the decay rate were a single exponential. The parameter β varies from 0 (linear ACF, zero slope) to 1 (exponential decay). For glass transitions, concentrated colloidal suspensions, concentrated polymer solutions, gels, and other complex fluids, where the ACF may cover many decades, a Williams-Watts function, while not necessarily theoretically applicable, is commonly used to simulate and to fit ACFs.

The simulator is useful for learning the correlator program even in the absence of a real signal. It also has uses in generating noisy data and testing how well different data analysis programs work. It may be useful for generating functions so they may be overlaid on real measurements. However, it is a violation of the scientific method to publish simulated data as if it were real, though the repeatability and accuracy of simulated data are quite good.

Section VIII: Screen Tour – Correlation Function Graph Window

To manipulate the correlation function graph window shown below, the command buttons in the toolbar are used. In this section of the manual the various features available in this toolbar are described. To follow the discussion, it is best to have the program running. The obvious features like Print and Clip (to clipboard) require no further discussion..

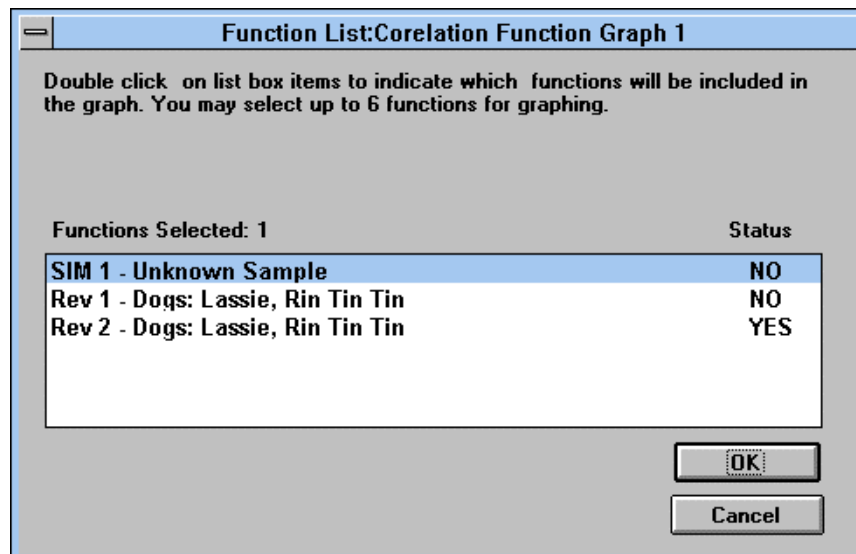


Function List

Up to six functions can be shown simultaneously on one graph. Click *Fn List* to determine which are displayed and which are not.

The functions are those in currently opened correlator control windows including:

- currently accumulating functions (input A and C, or multiple boards, for example),
- review windows (previously stored data),
- or simulation windows (for comparison purposes).



Order

If multiple functions are displayed, the order in which they are displayed and, therefore, the color in which they are displayed, can be controlled using the features accessed by clicking *Order*.

Cursor

To read out the values of each correlation point, click *Cursor*. Vertical and horizontal green cursor lines intersect at a particular channel. Use the mouse to move the cursor rapidly by clicking on a particular point in the ACF. Or, for finer control, click the right or left arrows in the cursor control box. The cursor control box is shown in the correlator control graph window on the previous page.

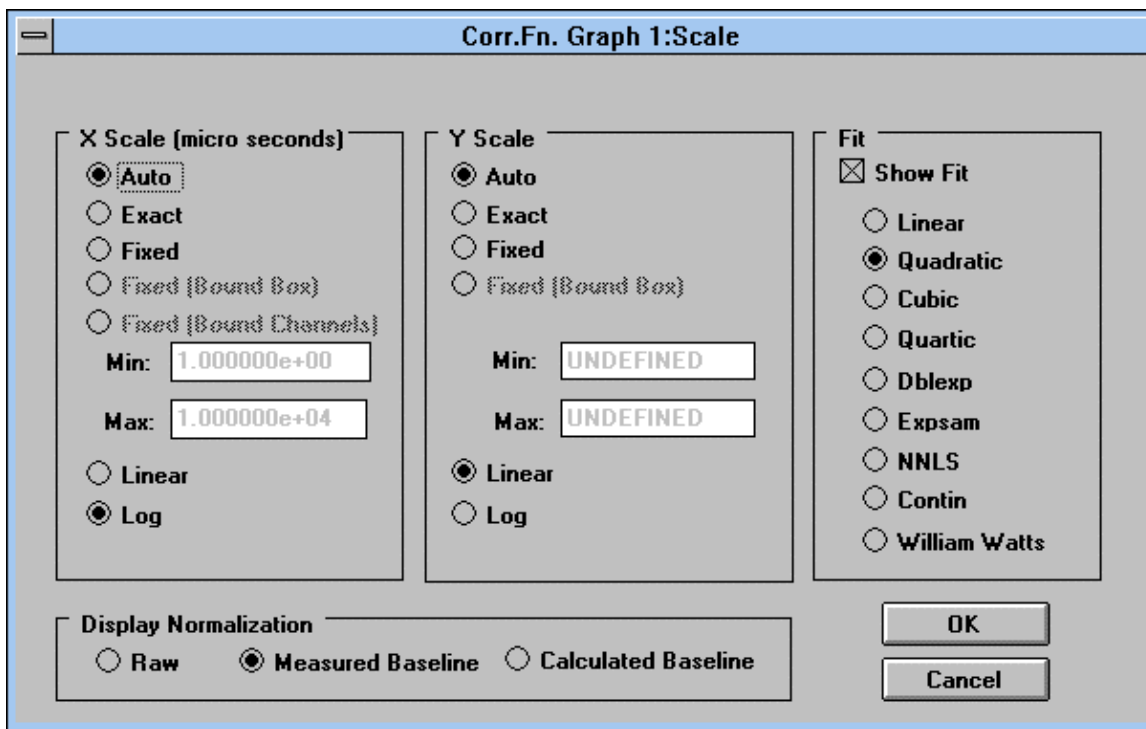
The information displayed in the cursor control box includes the channel number, the circuit (H for high, M for middle, and L for low speed circuit), the delay time, and the value of the autocorrelation function. The value will be between 0 and 1, if you have selected either **Measured** or **Calculated Baseline** in the Display Normalization section of the *Scale* window. The value will be a large integer, shown in scientific notation, if the **Raw Data** is selected in the Display Normalization section. This is the actual value in the channel, and it is this value that is used in all calculations as well as stored in data files.

[Do not confuse either the Measured or Calculated Baseline, used for display purposes only, with the equivalent choices in the Parameters command button in the correlator control window. Here, the baseline choice determines the display only; whereas, the baseline choice accessed from the Parameters command button determines the calculated results.]

NOTE: While the cursor is enabled a bound box cannot be created. A box is required for any of the following three purposes: to use the Zoom feature, to set the Measured Baseline to a particular group of channels, or to reset the first and last delays graphically. Click *Cursor* to hide the cursor and then use the mouse to draw a box.

Scale

Click on Scale to adjust the way in which the ACF is plotted.



Both the x and y axis values can be displayed linearly or logarithmically. Linear scaling of x and y yields the classic exponential decay function for diffusion measurements associated with particle sizing. Log scaling of x and linearly scaling of y yields the reverse S-shape curve common in multidecade correlators. Finally, linear scaling of y, log scaling of x, with either measured or calculated baseline normalization displayed, yields the classic straight line with negative slope for a monodisperse sample.

Autoscaling of the x axis uses the nearest decade in delay time, including extended channels, for display of the data. Exact scaling of the x axis uses the first and last delay time, or extended channels if enabled, for display of the data.

Autoscaling of the y axis allows one to observe the accumulation of the function as time passes. Exact scaling of the y axis sets the highest point obtained in hardware hardware to the highest point in the graph. Thus, with exact scaling the function will get smoother with time but it will not appear to accumulate.

Fit/Show Fit

Click in the Show Fit box. Click one of the fits: cumulants (linear, quadratic, cubic, quartic), double exponential, exponential sampling, NNLS, CONTIN, Williams-Watts. Or, use the hot key combination, Ctrl F, to turn this fitting feature on and off.

Correlation Function Graph: Page VIII-4

Fitted points are shown in the correlation function graph window as wide points. The fit is from the first delay to the delay that, after baseline normalization, remains positive. As the function builds, and becomes smoother and smoother, the number of fitted points in the tail of the function will typically increase.

If you choose a different baseline, the number of points fitted, as well as the fit itself, will change.

The fit is extrapolated at the high and low ends of the function, but these extrapolated values are shown as a thin line.

Showing the fit is just a convenience that is only useful when there are gross differences between the measured and fitted functions. The residual plots are much more sensitive to the quality of the fit. To access residual plots click on *ISDA/Residuals*, if you have that option.

Display Normalization

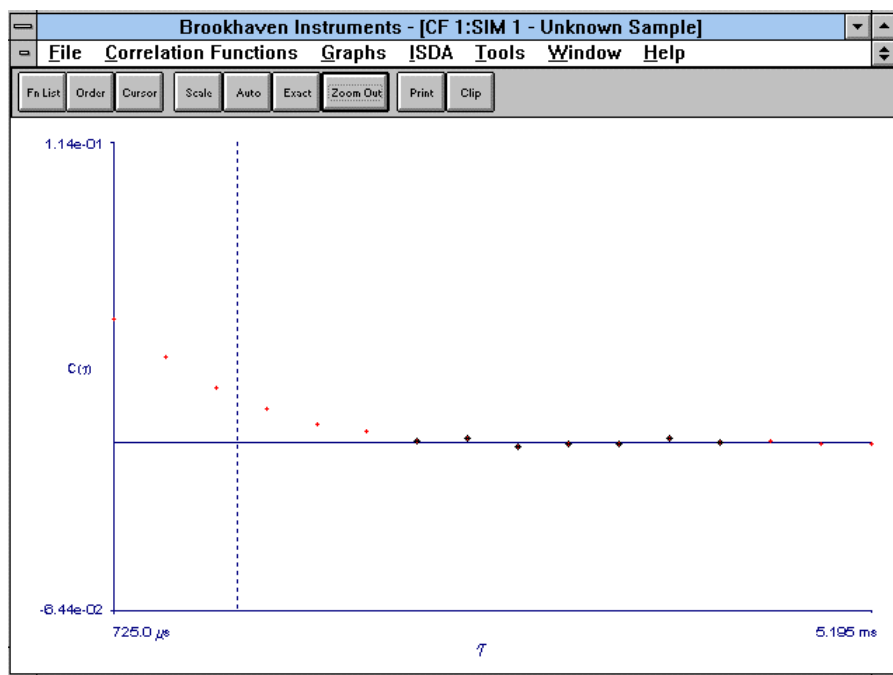
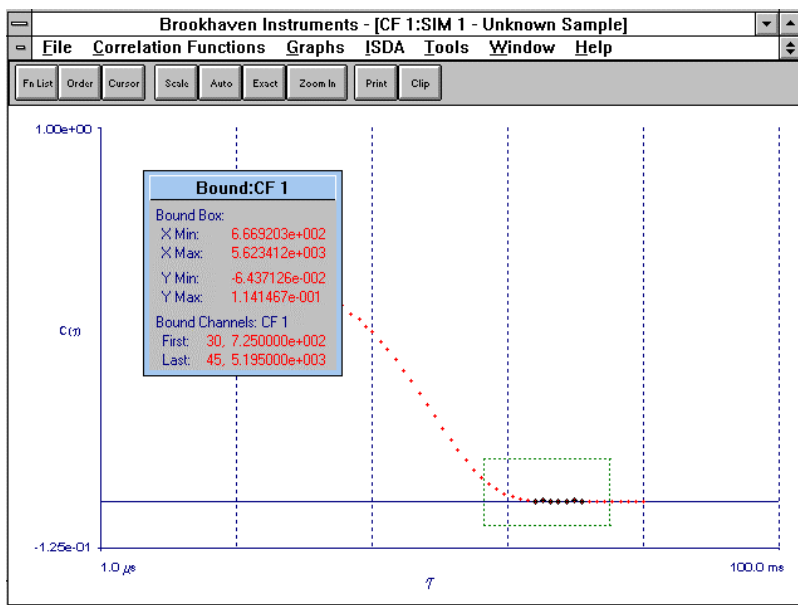
For display purposes only, select Raw, Measured, or Calculated Baseline. The raw data is always used for fitting data and is stored in the data files.

Auto/Exact

For display purposes only, auto and exact scaling are convenient. Thus, separate command buttons are available as well as the method described above. Here both axes are scaled simultaneously; whereas, using the *Scale* command button, each axis can be scaled separately.

Zoom In & Zoom Out

To temporarily view an expanded section of the ACF, use the mouse to click and drag a box around a section of the function. Notice that the zoom command button now says *Zoom In*. Click on *Zoom In*. This feature is useful for examining the tails of the ACF so that subtle changes in curvature are more apparent. Notice that the *Zoom In* button has now changed to *Zoom Out*. Click on *Zoom Out* to return to the full display.



Section IX: Data Analysis

General References

Much of the information in this chapter can be seen in greater detail in one or more of the following references:

1. **Laser Light Scattering**, authors Charles S. Johnson Jr. and Don A. Gabriel, Dover Publications, Inc., New York. This monograph, originally published in 1981 by the CRC Press was reissued in 1994 with corrections and added material. It is an excellent review of the earlier work including the frequency measurements before fast, digital correlators were available. Much of the emphasis is on biochemical applications, especially the early work from 1964 to 1980. A section on electrophoretic light scattering is also interesting.
2. Chapter 4, Data Analysis in Dynamic Light Scattering, Petr Stepanek, in **Dynamic Light Scattering: The Method and Some Applications**, author Wyn Brown, Oxford Science Publications, Clarendon Press, Oxford, UK, 1993. This chapter is an excellent review with references for all the popular data analysis methods up to circa 1991. Other chapters in this book cover scattering from polymer solutions, both dilute and semidilute, scattering from gels and other complex fluids. It is an excellent, advanced text with many good references on these subjects.
3. **Dynamic Light Scattering by Macromolecules**, author Kenneth S. Schmitz, Academic Press, 1990. Despite its title, this book covers static light scattering, scattering from colloids and complex fluids as well as emphasizing the title material.
4. **Laser Light Scattering: Basic Principles and Practice, Second Edition**, author Benjamin Chu, Academic Press, 1991. An excellent, overall presentation that includes many of the earlier experimental designs, the overlap of x-ray, neutron, and light scattering. There is material devoted to using single mode fiber optics in SLS and DLS.

Note that the BI-9000AT correlator was first available in February of 1992, and, as a result, none of these references refer to it. They do refer, however, to earlier Brookhaven correlators such as the BI-2030AT and the BI-8000AT.

Introduction to Data Analysis

The most common starting point in the analysis of the measured function, the second-order or intensity autocorrelation function (ACF) is the Siegert relationship:

$$G^{(2)}(\tau) = B \cdot \left(1 + f^2 |g^{(1)}(\tau)|^2 \right) \quad \text{IX-1}$$

Here $G^{(2)}(\tau)$ is the unnormalized measured function, sometimes designated as $C(\tau)$, where τ is the delay time. B is the baseline as determined by the infinite (calculated) delay time point, or one of several measured baselines (typically averaged over several delayed

values), or, occasionally, by fitting. The amplitude f is related to the temporal and spatial coherence properties of the laser beam and the detector optics. f is less than or equal to one and determines the intercept-to-baseline ratio. It is obtained during the fitting procedure and is here squared for convenience as it is always determined along with the normalized, first-order or electric field autocorrelation function $g^{(1)}(\tau)$. [Normalized correlation functions are traditionally shown as small g 's and unnormalized ones as capital G 's. Thus $g^{(2)} = G^{(2)}/B - 1$.] Physical parameters of interest are related to $g^{(1)}$ whereas the measured quantity is $G^{(2)}$.

The Siegert relationship is rarely violated except when there are very few scatterers in the scattering volume and when the system is non-ergodic. The validity of the relationship rests on the assumption that the scattered electric field is a Gaussian random variable, and that is ensured when there are many, say at least 30, scatterers in the intersection of the illuminated and detected volumes. [Note: Since the scattering volume is so small, 30 scatterers per scattering volume is typically $10^N/\text{volume}$, where N is 7, 8, 9 or 10. In other words, this is not a single particle counting technique!] When this criterion is violated, number fluctuations occur and there is an additional, slowly decaying term. For more information on this arcane topic, consult one of the references. In the Appendix D there is a short discussion of concentration and how to estimate the number of scatterers that contribute to the scattered light.

A system is ergodic when the ensemble average of a property (theoretically predicted) equals the time average of the property (measured). Except for gels and colloidal glasses, or in the case of very strongly interacting systems, or particles trapped in a network, ergodicity is assumed for the cases of interest here. Consult the references for information on these non-ergodic systems and how, in some cases, static light scattering is combined with the dynamic light scattering measurements to gain more information.

Note on Nomenclature

Over the years different authors have used different symbols. Early authors used the symbols we will employ in this chapter: τ for delay time; τ_r for decay time (see below); and superscripts enclosed in parentheses to designate first and second order autocorrelation functions such as $g^{(1)}$ and $G^{(2)}$. Later authors used t for delay time, τ for decay rate (especially in the polymer literature), and subscripts without parentheses to designate first and second order autocorrelation functions such as g_1 and G_2 .

Monodisperse, Rigid, Globular Scatterers

The references will show that, in this case,

$$|g^{(1)}(\tau)| = \exp(-\Gamma \cdot \tau) \quad \text{IX-2}$$

where Γ is called the decay or relaxation rate and $\tau_r = 1/\Gamma$ is called the decay or relaxation time. For dilute systems where the decay is entirely due to translational, diffusive motion of the center of mass of the scatterer, it can be shown that:

$$\Gamma = D_T \cdot q^2 \quad \text{IX-3}$$

where D_T is the translational diffusion coefficient and q is the magnitude of the scattering wave vector. This magnitude is given by,

$$q = \frac{4\pi n_1}{\lambda_0} \cdot \sin(\theta / 2) \quad \text{IX-4}$$

where n_0 is the refractive index of the liquid, λ_0 is the wavelength of the laser in a vacuum, and θ is the scattering angle. q^{-1} defines a length scale against which distances between scatterers is compared. When the distance is large compared to q^{-1} , then self-diffusion is measured. When the distance is small, then mutual diffusion is measured. Mutual and self-diffusion vary differently with concentration (particle-particle separation) depending on the attractive and repulsive forces involved. However, for very dilute samples, both asymptotically approach the same limit, $D_T \rightarrow D_0$, where D_0 is given by the Stokes-Einstein equation:

$$D_0 = \frac{k_B T}{3\pi\eta_l d_h} \quad \text{IX-5}$$

Here k_B is Boltzmann's Constant, 1.3807×10^{-16} ergs/deg, T is the absolute temperature in Kelvin, η_l is the bulk viscosity of the liquid in which the particle moves, and d_h is the hydrodynamic diameter of the assumed sphere.

Hydrodynamic diameters include the particle "dry" diameter plus whatever is permanently attached to, and moves with, the surface. In the case of hard mechanical spheres with relatively short-chain surfactants added to impart stability (e.g. 100 nm PS and sodium dodecyl sulfate, approximately 2 nm), the difference between the "dry" and hydrodynamic diameters is usually not significant. However, when the particle is much smaller and/or the attached species are much larger, as may be the case with polymer additives, then there can be a significant difference between the "dry" and hydrodynamic diameters. Interesting cases involve polyelectrolyte additives which exhibit isoelectric points. Such additives may significantly change size as a function of pH.

Self-Beating, Local-Oscillators, Homo/Heterodyning

In Eq. IX-1 it was assumed that only the scattered light mixed on the PMT to produce self-beating. This gives rise to the square term in $G^{(2)}$, and, in the case of a monodisperse system of rigid particles, the resulting $\exp(-2\Gamma \cdot \tau)$. If you use the BI-200SM goniometer, the 90Plus or the BI-MAS options on the ZetaPlus or ZetaPALS, the self-beat mode is obtained. If you use the FOQELS and the detected light does **not** include a significant portion of flare light from the cell wall, the self-beat mode obtains.

Imagine instead that a small fraction of the incident beam intensity was also mixed with the scattered light. This small fraction is called a local oscillator. It does not have the resulting time dependence of the scattered light. Provided that the strength of the local

oscillator is greater than approximately 5 to 10 times the scattered light, but not so great as to swamp the scattered light completely, $G^{(2)}$ varies in proportion to $g^{(1)}$ rather than its square. (In this case, the data analysis should proceed by fitting without taking the square root.) This is called the local oscillator mode and is rarely used except in the case of electrophoretic light scattering where the sign of the electrophoretic velocity is required.

However, unintentional stray light can also act as a local oscillator. This may occur, for example, in the FOQELS if the fiber optic probe is sufficiently far from the cell wall such that stray light from the illuminated cell wall contributes significantly to the detected light. For this reason, the user can analyze a collected function using either the self-beat or local oscillator settings. Click on the *Params* command button. Click on either *Self-Beating* or *Homodyne* (local oscillator).

In much of the DLS literature, and in the general references 1 and 2 cited at the beginning of this section, it is common to refer to the self-beat mode as homodyning and the local oscillator mode as heterodyning. In reference 4 it is pointed out that homodyning should refer to a local oscillator obtained from the same light source whereas heterodyning should refer to a local oscillator obtained from a different light source. Thus, most of the literature incorrectly refers to self-beating as homodyning and homodyning as heterodyning. These unfortunate misnomers are wide spread and the reader should be aware of them when comparing the literature to this manual and the program.

If the data is collected such that the self-beat mode dominates, analyzing the data using the homodyne selection will result in sizes **one half the expected values**.

In a more detailed analysis of the local oscillator mode one finds that the restriction of having a large number of particles is lifted. Thus, number fluctuations are no longer a problem in the local oscillator mode with a small number of particles. However, given the difficulty of setting a local oscillator correctly and the naturally low intercept-to-baseline ratio that results, the local oscillator mode is rarely used in practice except as noted above for electrophoretic and other velocity measurements.

In everything that follows it is assumed that the self-beat mode is used.

Model Fits

These include cumulants, Williams-Watts, and the double exponential, all of which are part of the optional BI-ISDAW package of fitting routines. There are more specialized fits (not currently offered by Brookhaven) for large polymer molecules, internal modes of motion, rotational diffusion, surface scattering (visco-elastic properties of surfaces), and motile micro-organisms. See reference 2 for details.

To access any particular fit, click on *ISDA* in the main window Menubar. If you do not see active choices, you may not have installed, or even purchased, the optional BI-ISDAW software.

Cumulants

The best known method for analyzing polydispersity is the method of cumulants first proposed by D.E. Koppel, *J. Chem. Phys.*, **57**, 4814, 1972. For an assumed continuous, normalized distribution of decay rates $G(\Gamma)$:

$$|g^{(1)}(\tau)| = \int_0^{\infty} G(\Gamma) \exp(-\Gamma \cdot \tau) d\Gamma \quad \text{IX-6}$$

and

$$\int_0^{\infty} G(\Gamma) d\Gamma = 1$$

For a discrete distribution of scatterers (particles or molecules), the distribution is written as,

$$\text{IX-7}$$

where I_i is the intensity scattered by, m_i is the mass of, and N_i is the number per scattering volume of the i th particle with decay rate Γ_i . Also, if the scatterers are molecules,

$$G(\Gamma) = \frac{\sum_i I_i \cdot \delta(\Gamma - \Gamma_i)}{\sum_i I_i} = \frac{\sum_i N_i m_i^2 P_i \cdot \delta(\Gamma - \Gamma_i)}{\sum_i N_i m_i^2 P_i} = \frac{\sum_i c_i M_i^2 P_i \cdot \delta(\Gamma - \Gamma_i)}{\sum_i c_i M_i^2 P_i}$$

readers will recognize that c_i is the mass concentration of

a polymer molecule with molecular weight M_i . The term $\delta(\Gamma - \Gamma_i)$ is the delta function and is used mathematically to select discrete values when integrated in Eq. IX-6.

The factor P_i accounts for angular scattering effects for particles larger than about $\lambda/20$, the usual approximation for non-Rayleigh scatterers. P_i is calculated from Mie scattering theory and requires the particles refractive index. For Rayleigh scatterers and at sufficiently low angles $P_i = 1$, and experienced readers will realize that the formalism above will lead to a z-average diffusion coefficient from which an inverse, z-average, particle diameter is calculated. More generally the averaging is by intensity and the resulting particle size is an inverse, intensity-weighted diameter. (It is sometimes claimed, incorrectly, that DLS measurements *always* yields a z-average result. This is only true when $P_i = 1$.)

Expanding the exponential in Eq. IX-6 about an average value, integrating term-by-term one obtains:

$$|g^{(1)}(\tau)| = \exp(-\bar{\Gamma}\tau) \cdot \left[1 + \frac{\mu_2}{2!} \cdot \tau^2 - \frac{\mu_3}{3!} \cdot \tau^3 + \frac{\mu_4}{4!} \cdot \tau^4 + K \right]$$

IX-8

Here the first moment about the origin is defined as

$$\bar{\Gamma} = \int_0^{\infty} \Gamma \cdot G(\Gamma) d\Gamma \quad \text{IX-9}$$

and the nth moment about this average value is defined as

$$\mu_n = \int_0^{\infty} (\Gamma - \bar{\Gamma})^n G(\Gamma) d\Gamma \quad \text{IX-10}$$

Taking the natural logarithm of equation IX-8, expanding in a Taylor series the term in brackets under the assumption that the sum of the various terms involving powers of τ is small, one gets the following simple polynomial (After adding back the amplitude f):

IX-11

$$\ln[f|g^{(1)}(\tau)] = \ln(f) - \bar{\Gamma}\tau + \frac{\mu_2}{2!} \cdot \tau^2 - \frac{\mu_3}{3!} \cdot \tau^3 + \frac{(\mu_4 - 3\mu_2^2)}{4!} \cdot \tau^4 - \dots \quad \text{K}$$

The coefficients of τ^n are known as cumulants, though

the first three are equal to simple moments.

The first moment, $\bar{\Gamma}$, is the most important term that is recovered. In polymer solutions it can be shown that (Doi and Edwards, The Theory of Polymer Dynamics, Clarendon Press, Oxford, U.K., 1986, page 107):

$$\bar{\Gamma} = D_T R_g^{-2} (qR_g)^n \quad \text{IX-12}$$

where, depending on the magnitude of qR_g , n is either 2 or 3. R_g is the radius of gyration, a measure of polymer size. It is proportional to $R_h = d_h/2$, the hydrodynamic radius, but not equal to it. When $n = 2$, simple center-of-mass diffusive motion occurs, and $\bar{\Gamma} = \bar{D}_T \cdot q^2$. This occurs in dilute solution where $qR_g \ll 1$. When $qR_g > 1$, $n = 3$; the motion observed in DLS is not diffusive; the internal polymer modes are probed; and $\bar{\Gamma}$ varies as q^3 . Furthermore, $\bar{\Gamma}$ is no longer dependent on the particle size or molecular weight.

For slightly concentrated systems the measured and infinitely dilute diffusion coefficients are expressed as:

$$\bar{D}_T = \bar{D}_o \cdot (1 + k \cdot c + K) \quad \text{IX-13}$$

This equation can also be applied to suspensions of particles as well. However, in more concentrated suspensions of particles or solutions of polymers the q^2 modes observed are

not proportional to self-diffusion but to mutual (cooperative) diffusion. Self- and mutual diffusion vary differently with concentration, and this is a topic beyond the scope of this presentation. Suffice it to say that it is wrong to interpret every ACF in terms of particle size derived from a self-diffusion coefficient.

Assuming the ACF can be interpreted in terms of self-diffusion, then for particle sizing the intensity-weighted self-diffusion coefficient is an average. After invoking the Stokes'-Einstein equation, Eq. IX-5, the following applies:

$$\text{Effective Diameter} \equiv \left(\frac{1}{\bar{d}_h}\right)^{-1} = \frac{\sum_i N_i d_i^6 P_i}{\sum_i N_i d_i^3 P_i} \quad \text{IX-14}$$

The **Effective Diameter**, abbreviated Eff. Dia., is neither the mass nor volume nor number-weighted diameters. Nor is it the intensity-weighted diameter. The intensity weighting is on the diffusion coefficient, and, since that varies inversely with particle size, Eq. IX-14 results. (Note: The d^6 term arises from the m^2 term in Eq. IX-7)

The Eff. Dia. is normally larger than most other common, average diameters since the averaging is over the 6th and 5th powers. In special cases, were P_i is a strong function of the angle, and a minimum in the Mie scattering pattern obtains, it is possible to observe a reversal such that the Eff. Dia. is smaller than the volume average diameter. But generally it is the other way around. This explains why dust and other, unwanted large particles, while few in number, can distort the results.

The second moment μ_2 is the intensity-weighted variance of the diffusion coefficient distribution when samples are dilute and interactions negligible. The relative variance, $\mu_2/\bar{\Gamma}^2$, which Brookhaven calls the **Poly** (short for polydispersity), is a measure of the width of the decay rate distribution, $G(\Gamma)$. [In early literature references this relative value is called the reduced second moment.] Therefore, when the distribution is one of particles, Poly is a measure of the size distribution width. It is an intensity-weighted relative variance of the diffusion coefficient, but nonetheless a measure of width. When the Poly equals zero, the sample is monodisperse, and as Poly increases so does the width of the distribution. It applies to monomodal as well as multimodal distributions since moments do not indicate distribution shape, only magnitudes. Sometimes that is enough since a sample such as a pure monoclonal antibody, a latex used as a reference material, or any other sample that is supposed to be narrowly distributed must have a low Poly, say less than 0.025.

The validity of the cumulant expansion rests on the assumption that the higher order terms do not contribute significantly. As a generalization it is found that the cumulant analysis works best when $\text{Poly} \leq 0.3$, approximately.

A relative third moment, defined in the ISDAW software as **Skew** = $\mu_3/(\mu_2)^{3/2}$, is a unitless number that can, if the skew is repeatable, indicate if the distribution is skewed to the left (negative skew) or to the right (positive skew) of the modal value.

A relative fourth moment, defined in the ISDAW software as **Kurtosis** = $\mu_4/(\mu_2)^2$, is a unitless number that, for unimodal distributions only, if repeatable, indicates the relative peakedness of the distribution compared to a Gaussian distribution (kurtosis = 3). The 4th moment obtained using the cumulant method is rarely of value and is included here for historic purposes only.

Using the Cumulant Fit

As explained previously, to open a cumulant window, click on *ISDA* and then on *Cumulant Analysis* and then on *New Window*. An example of what you might see is shown below:

	Gamma	Diff. Coef.	Eff. Diam. (nm)	Poly	Skew	Kurtosis	RMS Error	Amplitude
Linear:	2.627e+03	7.522e-08	65.2				1.1992e-03	0.642
Quadratic:	2.689e+03	7.697e-08	63.8	0.048			4.9335e-04	0.646
Cubic:	2.720e+03	7.788e-08	63.0	0.094	2.34		2.2873e-04	0.648
Quartic:	2.699e+03	7.727e-08	63.5	0.046	-7.89	-76.51	3.4107e-03	0.647

A standard polynomial least squares fitting procedure is used with weighting since the fit is of the logarithm rather than the directly measured value.

The various levels of fit are listed in the first column.

A linear fit just includes the linear term in τ . From the fitted Gamma, the diffusion coefficient can be calculated from Eq. IX-3 and IX-4. The Eff. Dia. is calculated from Eq. IX-5. To determine **Poly** requires at least a second order fit; to determine the **Skew** requires at least a third order fit; and to determine the **Kurtosis** requires at least a fourth order fit.

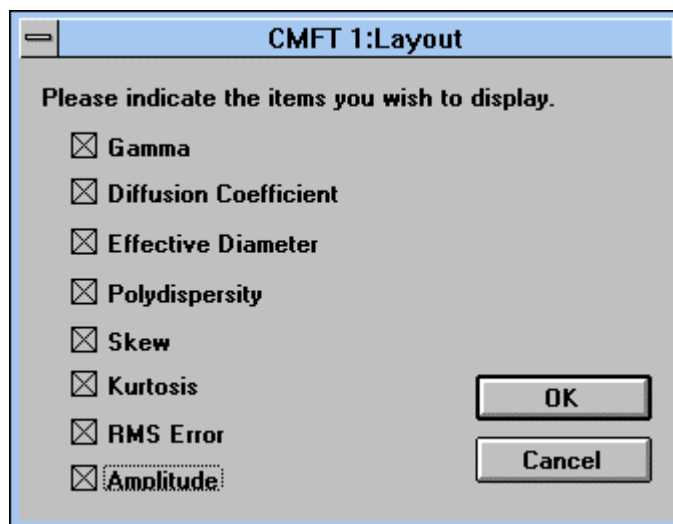
The RMS error is the root-mean-square error. It is the square root of the sum of squares of the differences between the fitted ACF and the measured. Before taking the square root the sum is divided by the number of data points minus the number of fitted parameters. The amplitude is f^2 as in Eq. IX-1. It represents the amplitude above the baseline chosen for the fit. The amplitude is a number between 0 and 1. Here the value of 0.64 means the detected and coherence areas were reasonably well matched.

A second order or quadratic fit yields the **Poly** from which distribution width can be decided. The results above show a **Poly** of 0.048 and a substantially lower RMS error, meaning the fit was significantly better. No doubt the sample is not monodisperse in this case.

The cubic and quartic fits are revealing. In this case neither is substantially better than the second order fit. Indeed, the RMS value for the fourth order fit is worse than the third order fit, and the various parameters actually reverse the trend from first through third.

This suggests that no more than three distribution parameters (ignore F) can be usefully determined. For example. If one of the other algorithms (CONTIN, NNLS, Exp. Sampling) yielded a bimodal (2 peaks plus the ratio of amount in each peak), this is consistent with three parameters. A trimodal is not consistent.

You need not display all of the fitted parameters. Click on *Display* in the Cumulant Fit (CMFT) window and you can select any or all of the following choices by clicking in the appropriate boxes:



Cumulant results are updated approximately every second depending on the speed of your computer and its memory. After the accumulation of the ACF has stopped, the results will also change if you change the baseline. If you change the parameters used in the calculations (temperature, viscosity, etc.), the first cumulant changes but not the **Poly**, **Skew**, or **Kurtosis** as they are ratios.

Higher order fits are not always worthwhile and may lead to large RMS errors if the data cannot support the forced fit. Look for trends that are repeatable and consistent with any prior knowledge of the scattering system.

Do not expect the cumulant method to work well when the distribution is very broad. This applies to broad particle size and polymer distributions, and it also applies to scattering from complex fluids and polymer solutions where more than diffusion is occurring.

Lognormal Approximation from Cumulants

While the method of cumulants is the oldest and still quite useful technique for analyzing ACFs, it cannot yield the shape of the decay rate distribution nor shed light on the shape of the size distribution. It can only yield, at best, moments of the distribution. A simple approximation, however, allows one to convert the first two moments into an intensity-weighted size distribution which can then be plotted. For particle size distributions a common unimodal choice is the Lognormal curve, which is a Gaussian or Normal curve in log space.

The n th moment of an x -weighted, Lognormal distribution of particle diameter is given by:

$$\overline{d_x^n} = d_{gx}^n \cdot \exp\left(\frac{n^2}{2} \cdot \ln^2 \sigma_g\right) \quad \text{IX-15}$$

where x determines the weighting (intensity, volume, surface area, number), d_{gx} is the geometric mean diameter with x weighting (also equal to the median value on a log scale), and σ_g is the geometric standard deviation (or harmonic standard deviation). A unique feature of a Lognormal distribution is that its width, characterized by the parameter σ_g is independent of the weighting.

The entire Lognormal curve by intensity is determined when d_{gI} and σ_g are specified. In the DLSW software we set Eff. Dia. = d_{gI} , and we calculate σ_g using the simplifying assumption that $P_i = 1$. The calculation is outlined as follows.

The Poly, Q , can be written as,

$$Q = \left(\overline{D_T^2}\right)_I / \left(\overline{D_T}\right)_I^2 - 1 \quad \text{IX-16}$$

where the I stands for intensity weighting. Using the definition in Eq. IX-5 and since the intensity I is proportional to $N \cdot d^6 \cdot P$, where P is the Mie scattering factor which reflects any angular dependence, one can relate Q to the intensity-weighted moments and thus to the Lognormal distribution. Further progress requires the values for P . Though strictly true only for Rayleigh scatterers or at low angles, the simplifying assumption that $P = 1$, allows one to derive the following simple formula relating the measured polydispersity index Q and the geometric standard deviation, σ_g :

$$\sigma_g = \exp\left\{\left[\ln(1+Q)\right]^{1/2}\right\} \quad \text{IX-17}$$

Please note that the Lognormal feature cannot possibly describe any multimodal distribution, nor one that is skewed on a log scale, nor was it intended as anything more than a way to visualize graphically the relative width as contained in Poly. The Lognormal distribution feature, and its assumptions stated above, may have value as a quality control tool only, nothing more.

For consistency with past programs, the value of Q (the Poly) used in Eq. IX-17 to determine the GSD is obtained from a second order fit only.

Williams-Watts

This function, also known as a stretched exponential, is useful when the ACF is a broad, non-exponential function such as those found when measuring complex fluids like viscous liquids and gels. For more information consult Section 2, Photon Correlation of Bulk Polymers, page 127, G.D. Patterson, **Light Scattering From Polymers**, Springer-Verlag, 1983.

The Williams-Watts function is given as

$$|g^{(1)}(\tau)| = \exp\left[-\left(\frac{\tau}{\tau_r}\right)^\beta\right] \quad \text{IX-18}$$

where $0 < \beta \leq 1$ describes the width of the distribution of relaxation times τ , and τ_r is a characteristic relaxation time. When $\beta = 1$, the distribution is exponential, but as β approaches zero the decay in the ACF covers many decades.

An average decay rate can be calculated by integrating Eq. IX-18 multiplied by τ . The result is:

$$\bar{\tau} = \frac{\tau_r}{\beta} \cdot \Gamma\left(\frac{1}{\beta}\right) \quad \text{IX-19}$$

Here $\Gamma(1/\beta)$ represents the gamma function tabulated in statistical textbooks, not the linewidth associated with the decay of an ACF.

The Williams-Watts function is interesting in that it attempts to fit the $g^{(1)}$ function directly rather than a size distribution.

Using the Williams-Watts Function

To invoke the W-W fit, click on *ISDA*, then on *Williams-Watts*, and finally on *New Window*. An example of what you might see is shown below:

Parameter	Value
Amplitude:	0.643
Linewidth, $\Gamma = 1/\tau_R$:	2.617e+03
Relaxation Time, τ_R :	3.821e-04
Width Parameter, β :	9.940e-01
RMS Error:	1.026e-03

The W-W function is fit to the data using a non-linear least squares approach, a standard Levenberg-Marquardt algorithm. No weighting is required. If the problem had been linearized before fitting, by taking the log of the log, weighting would be required. The log of the log is notorious for removing much of the interesting variations in a function and, sometimes, leads to results devoid of much physical meaning. Indeed, one must approach the W-W fit as a convenient numerical fit to the data as fundamental theory showing the appropriateness of the W-W equation is, at the present time, sparse.

Double Exponential (D.E.)

Like the W-W and cumulant fits, the D.E. fit assumes a particular form for the first-order ACF, namely:

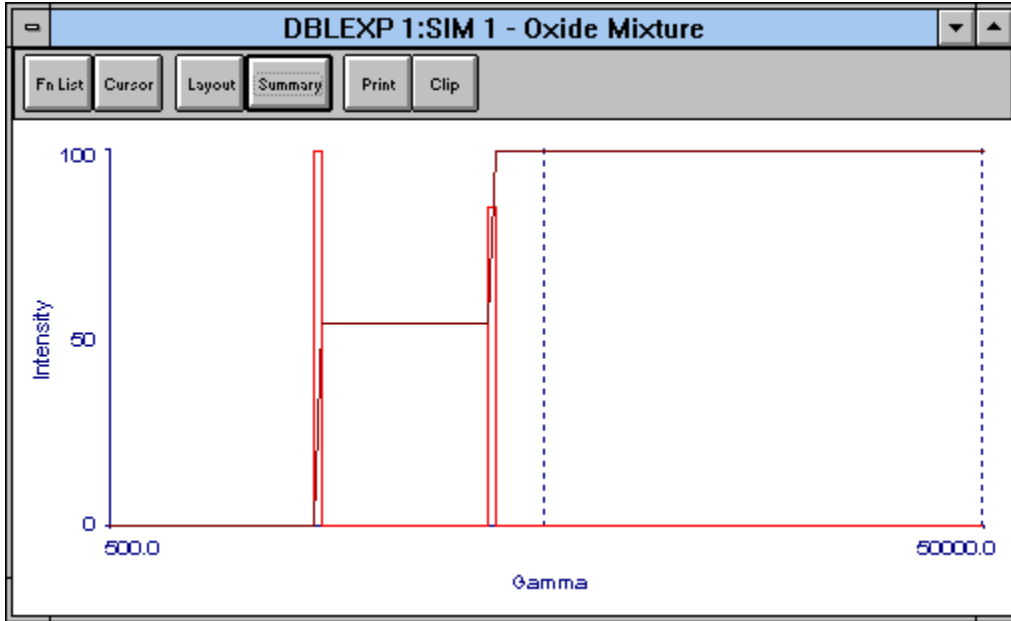
$$|g^{(1)}(\tau)| = G(\Gamma_1) \cdot \exp(-\Gamma_1 \tau) + G(\Gamma_2) \cdot \exp(-\Gamma_2 \tau) \quad \text{IX-20}$$

where $G(\Gamma_i)$ represents the relative intensity contributed by the i th scatterer with decay rate Γ_i . This too is a non-linear least squares problem for which the Marquardt-Levenberg algorithm is used.

Note that this is a force fit: do not be surprised if a double exponential results. One can fit some very broad but unimodal distributions using the double exponential. Nothing can be said about the actual distribution shape when force-fit to a double exponential. The global mean and global variance, as determined by both resulting peaks, are useful for characterizing moments of, but not for determination of, the true distribution shape. One could not say, for example, because the RMS error is small that the distribution is therefore actually a double exponential.

Using the Double Exponential Fit

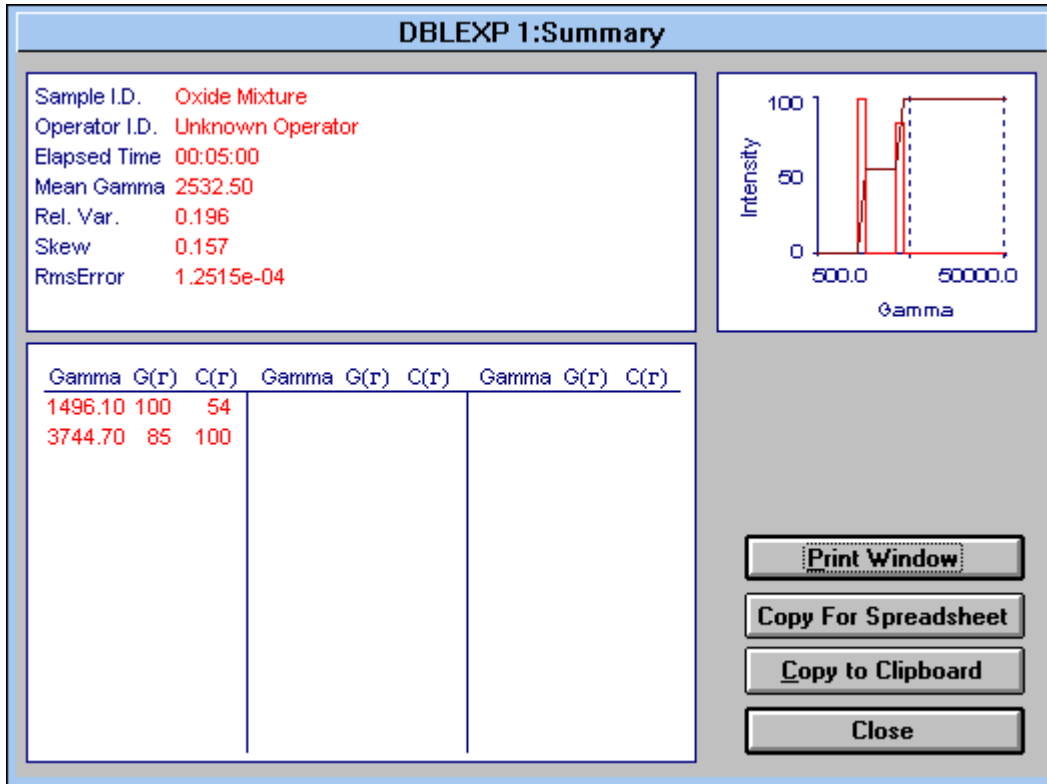
To invoke the D.E. fit, click on *ISDA*, then on *Double Exponential*, and finally on *New Window*. An example of what you might see is shown below:



The vertical bars are centered at Γ_1 and Γ_2 . The thickness of the bar has no meaning. It was chosen only for display purposes. The relative heights of the bars represent $G(\Gamma_1)$ and $G(\Gamma_2)$. The single line starting at zero, connecting the bars, and eventually rising to 100 represents the cumulative distribution of the relative intensity-weighted Γ distribution.

Click on *Cursor* to reveal a small, inset window. Either click in the graph or on the black arrows in the inset box to move the vertical cursor line. Values of Γ , $G(\Gamma)$, and $C(\Gamma)$, the latter representing the cumulative distribution, are displayed.

Alternatively, for a list of these values and the calculation of the moments resulting from them, click on *Summary* to see the following:



The kth value of the cumulative undersize function, C, is calculated from the histogram values G as follows:

$$C(x_k) = 100 \cdot \frac{\sum_{i=1}^k G(x_i)}{\sum_{i=1}^N G(x_i)} \quad \text{IX-21}$$

where the values of C(x) are rounded to the nearest whole percent and N is the total number of entries. For D.E. I = 1, 2 and N = 2. The variable x can represent either the decay rate Γ , or its inverse the relaxation time τ_r , or a diameter d calculated from Γ and Eqs. IX-3, -4, and -5. The other statistical parameters are calculated as follows:

$$\text{Mean of } x = \bar{x} = \frac{\sum_{i=1}^N x_i G(x_i)}{\sum_{i=1}^N G(x_i)} \quad \text{IX-22}$$

$$\text{Variance of } x = \sigma^2 = \frac{\sum_{i=1}^N (x_i - \bar{x})^2 G(x_i)}{\sum_{i=1}^N G(x_i)} \quad \text{IX-23}$$

$$\text{Third moment} = \mu_3 = \frac{\sum_{i=1}^N (x_i - \bar{x})^3 G(x_i)}{\sum_{i=1}^N G(x_i)} \quad \text{IX-24}$$

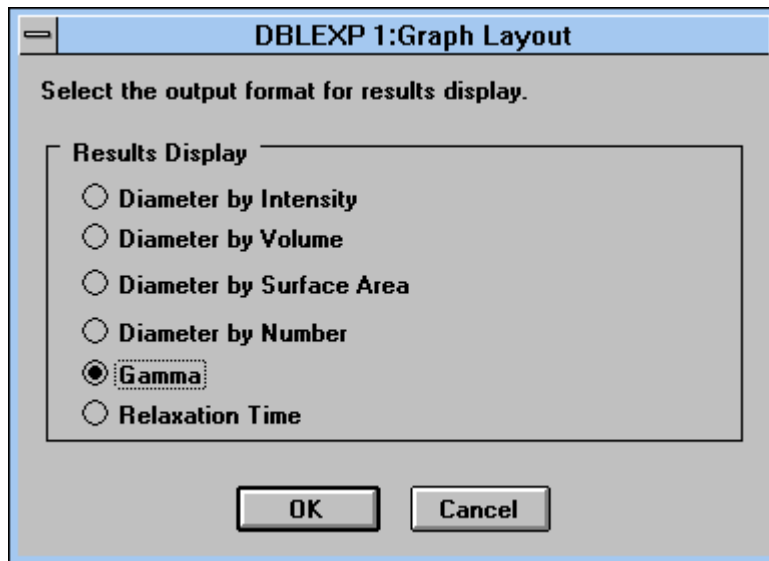
The **Rel. Var.** $\equiv \sigma^2 / (\bar{x})^2$ and the **Skew** $\equiv \mu_3 / \sigma^3$. See page IX-8 for the definition of RMS error. All of these values are shown in the summary.

Please note that the double exponential fit does not always converge. It depends on the noise and shape of the ACF as well as the initial guesses. For the initial guesses the ACF is first fit to a second order cumulant producing $\bar{\Gamma}$ and μ_2 . Then the initial guesses are as follows: $G(\Gamma_1) = G(\Gamma_2) = 0.5$, $\Gamma_1 = \bar{\Gamma} + \sqrt{\mu_2}$, $\Gamma_2 = \bar{\Gamma} - \sqrt{\mu_2}$.

Double Exponential Presentation: Relaxation Time, Particle Size

Starting with Eq. IX-20, the presentation above covered the intensity weighting of the decay rate. But Eq. IX-20 could have been written in terms of relaxation time $\tau_r = 1/\Gamma$. The results are obtained from the Γ -fit as follows: $\tau_{r1} = 1/\Gamma_1$, $\tau_{r2} = 1/\Gamma_2$, $G(\tau_{r1}) = G(\Gamma_1)$, and $G(\tau_{r2}) = G(\Gamma_2)$. The mean, relative variance, and skew are then calculated from Eqs. IX-22, -23, and -24. The cumulative distribution is calculated from Eq. IX-21.

To select the relaxation time output or the size distribution output, click the *Layout* button in the Double Exponential window accessed from the ISDA menu. It is reproduced below.



Click on *Diameter by Intensity* to see a particle size distribution weighted by the intensity of scattered light. The results are obtained from the Γ -fit as follows: $d_1 = c/\Gamma_1$, $d_2 = c/\Gamma_2$, $G(d_1) = G(\Gamma_1)$, and $G(d_2) = G(\Gamma_2)$. The mean, relative variance, and skew are then calculated from Eqs. IX-22, -23, and -24. The cumulative distribution is calculated from Eq. IX-21. Here the constant c is $(k_B T/3\pi\eta) \cdot q^2$, where q is defined in Eq. IX-4.

Click on *Diameter by Volume* to see a particle size distribution weighted by the volume of particle sizes with a given diameter d . If the particles all have the same density, then this distribution is equal to the mass-weighted size distribution. For historical reasons, a mass-weighted distribution is often referred to as the weight distribution. The results are obtained from the intensity-weighted distribution $G_I(d)$ by forming the unnormalized volume-weighted value $G_V(d) = G_I(d)/(d^3 P(\theta))$, where $P(\theta)$, the angular part of the Mie scattering coefficient, is calculated using a modified version of the program BHMIE for homogeneous spheres found in the appendix of the book **Absorption and Scattering of Light by Small Particles**, authors C.F. Bohren and D.R. Huffman, Wiley-Interscience publishers, 1983. A normalized version, G'_V , is obtained by setting the highest value of G'_V equal to 100.

Given the set of $G_V(d)$, the mean, relative variance, and skew are then calculated from Eqs. IX-22, -23, and -24. The cumulative undersize distribution is calculated from Eq. IX-21.

Click on *Diameter by Surface Area* or *Diameter by Number* to obtain surface area-weighted $G_S(d)$, or number-weighted size distributions $G_N(d)$. These are related to volume-weighted distribution as follows: $G_S(d) = G_V/d$ and $G_N(d) = G_V/d^3$. Then normalized versions of G_S and G_N are calculated from the unnormalized versions. Again, once the sets of $G_S(d)$ and $G_N(d)$ are known, the respective means, relative variances, and skews are then calculated from Eqs. IX-22, -23, and -24. The cumulative undersize distributions are calculated from Eq. IX-21.

It bears repeating: Just because the RMS and residual plots —channel-by-channel comparisons of the fitted and measured ACFs— indicate good agreement does not mean that the distribution is bimodal. Historically, the difficulty in getting good D.E. fits was the first indication that fitting sums of exponentials from DLS data was much more involved than first expected.

Appendix A: Data File Formats

Data files in the *Database* are stored in binary, readable only with a copy of the BI-DLSW program. When you *Archive* and *Reload Archived* files you are doing so in the binary format. We suggest archiving all important data files periodically onto separate media, stored safely away from the lab in which the system is used in case the computer or hard drive stop working, or in case of fire or other mishap.

However, you can also **Export** and **Import** data files, called here raw data files, that will then be readable by the BI-9000AT DOS software. In addition, these ASCII files can be used to analyze the correlation function with user-supplied programs. Exported files use the extension .dat; otherwise you are free to set the path and the filename.

Raw Data File Formats

1. Run Number
2. Total Counts, A Input
3. Total Counts, B Input
4. Number of Samples
5. not used
6. First delay in microseconds
7. Number of data channels
8. Determines whether the ISDA programs will prompt the user for which baseline to use:
 - 0 = will prompt
 - 1 = use calculated baseline
 - 2 = use measured baseline
- . The numbers 1 or 2 will only occur if the file was created by a control file in the DOS software or by a Cmm script in the DLSW software
9. Angles
10. Wavelength in nanometres
11. Temperature in degrees Kelvin
12. Viscosity in centipoise
13. not used
14. Refractive index of liquid
15. Refractive index of particle/polymer, real part
16. Refractive index of particle/polymer, imaginary part
17. One less than the number of parameters preceding the x and y data in this file. As of the date of this document, April 23, 1998, the number of parameters is 37.
18. First channel used for calculations
19. Time delay mode
 - -2 = Constant ratio spacing
 - -1 = Spacing from delay file
 - 1 = Linear spacing
20. Analysis mode

- 2 = Autocorrelation
 - 3 = Cross correlation
 - 4 = Test
21. Number of extended baseline channels
 22. Calculated baseline
 23. Measured baseline
 24. Last delay in microseconds
 25. Sampling time used to generate number of samples (μs)
 26. First delay used from High speed section
 27. Number of High speed channels used
 28. Middle speed sampling time (μs)
 29. Number of Middle speed channels
 30. Low speed sampling time (μs)
 31. Number of Low speed channels
 32. not used
 33. not used
 34. not used
 35. First measured baseline channel number
 36. Last measured baseline channel number
 37. not used
 38. Delay Time #1 Channel Contents #1
 39. Delay Time #2 Channel Contents #2
 40. Delay Time #3 Channel Contents #3
 41. Delay Time #4 Channel Contents #4
 - . .
 - . .
 - . .
 - . Sample ID
 - . Operator ID
 - . Date
 - . Time

Appendix B: Delay Files

Delay files can be created by the user, stored in the path `c:\bicw\dlyfil`, and given the extension `.dly`. Delay files can then be recalled by file name from the correlator control window *Layout* command key. Delay files allow the user complete freedom to layout correlator channels subject only to the hardware limitations. A properly designed dly file must be used, for example, to achieve the maximum number of total channels, which is 522.

Rules for Delay Files

All files must begin with the line: BI9KDLY.

HS, MS, and LS stand for, respectively, high speed, middle speed and low speed circuits.

1. If HS installed, create an ASCII file with this section of code:

```
BI9KDLY
:H
0.025    [displays all HS channels from 0.025, 0.05, ..., 2.4 μs]
```

OR

```
BI9KDLY
:H          [if HS not installed, displays 0.100, 0.200, ..., 2.4 μs]
```

2. MS notation in ASCII file looks like following:

```
:M
I N B      I=0,1,2,...7  Index to set SAMPLING TIME
```

N sets total number of channels, including base channels.
maximum depends on the Index

B = 0....8 sets number of baseline channels

I = 0	0.5 μs	N = 20 , max for 100% efficiency
I = 1	1.0	N = 40
I = 2	2.0	N = 80
I = 3	5.0	N = 160
I = 4	10.0	N = 256, max limited by software
I = 5	20.0	N = 256
I = 6	50.0	N = 256
I = 7	100.0	N = 256

An Example of a Delay file using the HS and MS speed Circuits:

Problem:

1. Display all standard HS channels starting from 100 ns
2. Display 37 correlation + 3 base channels in the MS section, starting with a delay time of 1.5 μ s and the last delay time before the baseline channels at 64 μ s.
3. Put the first of the 3 baseline channels at 250 μ s.

One Possible Solution:

Use :H since want all standard HS channels: 100, 200 ns, etc.
 N = 40, B = 3
 For MS section to start at 500 ns, I = 0 (see table above)

```
BI9KDLY
:H
:M
0 40 3           ( I N B, here I=0, N=40, B=3)
3 4 5 6 7 8 9 10 11 12
14 16 18 20 22 24 26 28 30 32
36 40 44 48 52 56 60 64 68 72
80 88 96 104 112 120 128 500 501 502
```

The integers in the rows below I N B represents the multipliers of the basic sampling time of 0.5 μ s. For example, the first three delay times are 3•0.5, 4•0.5, and 5•0.5 or 1.5, 2, and 2.5 μ s. The delay times for the last two of the 37 contiguous channels are 120•0.5 and 128•0.5 or 60 and 64 μ s. The three baseline channels are at 500•0.5, 501•0.5, and 502•0.5 or 250 μ s, 250.5 μ s, and 251 μ s.

Note that this is one possible solution that satisfies the stated goals of the problem, because the multipliers were somewhat arbitrary. One could have used multipliers 13, 21, and 62 instead of 12, 20, and 60, for example. There would still be 37 contiguous channels, but the spacing would be a little different. There are a very large number of ways of laying out the channels.

Note also that more than 20 contiguous channels have been used in the MS section even though the sampling time is 0.5 μ s. This means that the collection of data, while satisfying the stated goals, is not 100 % efficient. Using the *Layout* command key in the correlator control window, this particular layout would be impossible, in part because 100% efficiency is the constraint used in the automatic algorithm. Using delay files one can trade off efficiency for a particular layout.

The example above should be given a name, for example, 64us.dly, and stored in c:\bicw\dlyfil.

3. MS notation in ASCII file looks like following:

```
:L
I N B      I=0,1,2,...9  Index to set SAMPLING TIME

           N sets total number of channels, including base channels.
           maximum depends on the Index

           B = 0....8  sets number of baseline channels
```


I = 0	0.05 ms	N = 120 , max for 100% efficiency
I = 1	0.1	N = 240
I = 2	0.2	N = 240
I = 3	0.5	N = 240
I = 4	1	N = 240
I = 5	2	N = 240
I = 6	5	N = 240
I = 7	10	N = 240
I = 8	20	N = 240
I = 9	40	N = 240

An Example of a Delay file using the HS, MS, and LS speed Circuits:

Problem:

1. Display all standard HS channels starting from 100 ns
2. Display 40 MS channels using a 1 μ s sampling time, starting from a 3 μ s delay time and ending at 176 μ s.
3. Display 18 LS channels using a 2 ms sampling time, starting from a 2 ms delay time and ending at 256 ms.
4. Display 2 baseline channels using the LS circuit such that the first one is at 2 s.

One Possible Solution:

```

:H
:M
1 40 0 <----- index 1 = 1 usec sample time
3 4 5 6 7 8 9 10 11 12 <----- multipliers for MS sample time (=1  $\mu$ s)
14 16 18 20 22 24 26 28 30 32
36 40 44 48 52 56 60 64 68 72
80 88 96 104 112 120 128 144 160 176
:L <----- setup for low speed
5 20 2 <----- index 5 = 2 ms sampling time
1 2 3 4 6 8 10 12 16 20 <----- multipliers for LS sample time (=2 ms)
24 28 32 40 48 56 64 128 1000 1100

```

Note that the MS section ends at 176 μ s while the LS section doesn't start until 2 ms. By design, there is a gap between the delay times from 176 to 2,000 μ s. This demonstrates the complete flexibility one has in designing layouts using the BI-9000AT and delay files.

Appendix C: Scripting Files, Cmm

A very powerful scripting language is available for automating the correlator; however, the document describing that language is too large to include here. If you require Cmm documentation, please contact the factory and we will send you a copy.

Cmm Introduction

The Cmm language is an interpreted language based on a streamlined version of C. It has a simplified syntax that does not require pointers or declarations. The purpose of including the interpreter in this software is to provide a mechanism for the user to automate correlator data collection sequences. Typically, the user will execute a script that will automate a sequence such as sweeping a goniometer through a list of pre-defined

angles, stopping to collect correlation functions along the way, which are saved to the database for future analysis.

Appendix D: Scattering Volume, Concentrations, & Particle Interactions

In a typical DLS experiment, one using lenses and pinholes, a nominal 1 mm laser beam is focused to approximately 100 μm . The focusing is such that, over the length of the detected region, the beam can be modeled as a cylinder. [Focused laser beams are hyperboloids of revolution, but one usually chooses the focusing optics such that the cylindrical approximation is reasonable.] A common detection scheme might look at a 200 μm length of the cylinder at a 90° scattering angle. The resultant scattering volume $V_{\text{scatt}}(90) \approx 1.6 \times 10^{-6} \text{ cm}^3$. At other angles, with the optics fixed, the length of the scattering volume observed is larger by an amount that varies inversely with the sin of the scattering angle. Thus $V_{\text{scatt}}(\theta) \approx 1.6 \times 10^{-6} \text{ cm}^3/\sin(\theta)$, doubling in volume at 30° and 150° , quadrupling in volume at 15° .

In statistics a common assumption is that at least 30 values are needed for Gaussian statistics to apply. Assume that the minimum number of scatterers per scattering volume is 30 for the Siegert relationship to apply, though experimentally one finds a minimum more like 10 times that number. What does this mean for the concentration?

Let $C_n \equiv$ (Number of Particles/Unit Volume). Then $C_n(\text{min}) \approx 30/1.6 \times 10^{-6} \text{ cm}^3 \approx 1.9 \times 10^{+7}$ particles/ cm^3 . This means that DLS measurements are ensemble average measurements over large numbers of particles; they are not single particle measurements. For this reason alone a DLS determination of the particle size distribution is no substitute for a single particle counter *if an accurate measurement of the number distribution is required*.

More often the concentration of interest is either the volume fraction $\phi_v \equiv$ (Volume of Particles/Unit Volume), which, for a monodisperse dispersion is given by $\phi_v \equiv v_p \cdot C_n$, or the weight/volume concentration $C_w \equiv$ (Mass of Particles/Unit Volume) = $\rho_p \cdot \phi_v$. Here $v_p = (\pi/6) \cdot d^3$, the volume of a single particle, and ρ_p is the particle density of a spherical particle of diameter d . Minimum concentrations for a range of sizes is then given by:

d (nm)	$\phi_v(\text{min})$	$C_w(\text{min}, \rho_p = 1 \text{ g/cm}^3)$
10	$10^{-11} \text{ v/v} = 10^{-9} \%$	$10^{-11} \text{ w/v} = 10^{-9} \%$
100	$10^{-8} \text{ v/v} = 10^{-6} \%$	$10^{-8} \text{ w/v} = 10^{-6} \%$
1000	$10^{-5} \text{ v/v} = 10^{-3} \%$	$10^{-5} \text{ w/v} = 10^{-3} \%$

Experience with real samples suggests a minimum volume concentration of $10^{-5} \%$ for 100 nm particles in accordance with the suggestion above that while 30 particles may be the minimum for Gaussian statistics and the Siegert relationship to apply, something like 10 times that number is required for realistic measurements.

For concentrations lower than those in the table, one can expect number fluctuations. See the very brief discussion on this subject in the section on data analysis and consult the references at the beginning of that section.

Scattering Volume & Concentration: Appendix D-2

Another aspect of DLS applied to particle sizing may be illustrated using the table above. To calculate particle size from the diffusion coefficient, it is assumed that the Stokes-Einstein law applies. Therefore, it is assumed that the particles do not interact. This is certainly true in dilute suspensions. In the case of particles electrostatically stabilized, interactions may be minimized, even at higher particle concentrations, by shielding the particles using a diluent consisting of 10 to 30 mM, 1:1 electrolyte. Note, however, adding too much salt can have the opposite effect: collapsing of the electrical double layer, resulting in flocculation or aggregation. But this effect normally occurs well above 100 mM of 1:1 electrolyte.

As a crude guess, let us assume that when the center-to-center distance between particles, L , is greater than 20 times the particle diameter, d , that they do not interact. A crude model of a suspension might assume, on average, something less than the 12 nearest neighbors in a close-packed crystalline structure such as a face-centered cubic or a hexagonal closest packed unit cell. Such a model leads to a simple relationship between the volume fraction and the ratio of d/L . Depending on the number of nearest neighbors, the relationship is given by $\phi_v(\max) = b \cdot (d/L)^3$, where $b = 0.74$ for a closest packed crystalline structure with 12 nearest neighbors, and $b = 0.5$ with a loose, amorphous structure with 6 nearest neighbors.

Assuming $d/L < 0.05$ is reasonable for noninteracting particles, this leads to a $\phi_v(\max)$ of $6.3 \times 10^{-3} \%$. This value is only 6.3 times as large as the $\phi_v(\min)$ for a $1 \mu\text{m}$ particle, assuming a minimum of 30 particles in the scattering volume. So the range of concentrations from the minimum to the maximum is 6.3. However, if the minimum number of particles is more like 300, as it is for much smaller particles, then it is literally impossible to satisfy the two opposing criteria.

Thus, while it is easy to satisfy the opposing concentration criteria—at least 30 to 300 particles in the scattering volume but not so many that the particles interact—with the smaller diameter particles, it becomes increasingly difficult if not impossible to do so as particles above $1 \mu\text{m}$ or so are considered.

Particles above this size range scatter more and more in the forward direction, making it difficult to measure since alignment and dust are significant problems in the forward direction. Also, larger particles may sediment during the measurement. They also diffuse more slowly, requiring much longer measurement times. Yet, the violation of the Siegert relationship is as fundamental to the breakdown of DLS above this size range as any of the other effects. For these reasons, particle sizing above, very approximately, $1 \mu\text{m}$ using DLS is not easy to justify.

[Note: While one could increase the focused beam diameter to allow a greater number of particles in the scattering volume, the power per coherence area decreases, and this leads to much reduced intercept/baseline ratios. Repeatability suffers and it becomes nearly impossible to obtain reliable second moments as the rise above the baseline in the tail of the ACF is barely perceptible above the noise. In addition, increasing the beam diameter increases the chances of a dust particle crossing the beam during the measurement. And when it does, it has a longer illuminated path in which to travel.]

Appendix E: Multiple Correlator Boards in a Single Computer

Multiple 9000AT correlator boards can be used with one computer and controlled by the DLSW software. The following is valid only for the ISA cards. PCI cards need to get specific EPROMS due to the Plug 'n Play address relocation mode.
Contact the factory for new EPROMS

Boards are numbered from 0 (zero) to 7 (eight boards maximum).
The "zero" board is the "first" and in most cases the only board.
"x" : jumper is installed
"-" : no jumper

Set the jumper on each board as follows:

	<u>Jump22</u>	<u>Jump21</u>	<u>Jump20</u>	<u>Base Hex address</u>
Board 0	-	-	-	0300
Board 1	x	-	-	0302
Board 2	-	x	-	0304
Board 3	x	x	-	0306
Board 4	-	-	x	0308
Board 5	x	-	x	030A
Board 6	-	x	x	030C
Board 7	x	x	x	030E