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p.25

DEVELOPMENT OF A VERSATILE LASER LIGHT SCATTERING INSTRUMENT

by

William V. Meyer

and

Rafat R. Ansari

NASA Lewis Research Center
Case Western Reserve University
Cleveland, Ohio

Submitted as a Final Report on Cooperative Agreement NCC3-74
to the NASA Lewis Research Center Technical Officer
Cleveland, OH 44135

October 1990

Case Western Reserve University
Cleveland, OH 44106

LASER LIGHT SCATTERING CAPABILITIES

A modular approach for assembling a laser light scattering instrument from basic building blocks (Optical Lego) will allow us to implement dynamic light scattering, static light scattering, dynamic depolarized laser light scattering, etc. in a manner ideal for each of NASA's Principal Investigators. Dynamic light scattering, as used in this report, is a digital technique for measuring and correlating the intensity fluctuations in the scattered light that arise from the Brownian motion of particles in the sample. This gives the diffusion coefficient from which particle sizes in the range of 3 nanometers to above 3 microns are determined. Static light scattering - the measurement of time-averaged intensity scattered by dispersions of particles and macromolecules (e.g. polymers, proteins, micelles, microemulsions, etc.) - is an important tool for the determination of particle structure, weight-average molecular weight and particle interactions. Dynamic depolarized laser light scattering is different from regular dynamic light scattering in that it examines the weak, horizontally polarized scattered light coming from the sample. This depolarized signal contains dynamic and structural information which is not otherwise readily available.

JUSTIFICATION

NASA Lewis Research Center is developing and coordinating the development of a versatile light scattering instrument for use in microgravity. Laser Light Scattering (LLS) will be used in microgravity to measure microscopic particles of 30 angstroms to above 3 microns. Since it is an optical technique, LLS does not affect the sample being studied.

Critical phenomena, nucleation, spinodal decomposition, gelation, aggregation, diffusion, etc. are influenced by gravity and can be better studied with LLS in a microgravity environment. LLS can enhance protein crystal growth experiments which need quantitative information about the growth process and an indication of the onset of nucleation. The above experiments and many others have already been presented to NASA in the form of "pre-proposals", which were solicited by this ATD project from experts in the field desiring an opportunity to use LLS in microgravity. A number of very well qualified investigators have identified a group of basic science experiments which require microgravity for their performance and which will be enabled by LLS instrumentation. These potential Principal Investigators (PIs) will be responding to the Laser Light Scattering section of NASA's forthcoming Announcement of Opportunity (AO) when it is released at the end of 1990.

PROGRAM OBJECTIVES

The major objectives of this Advanced Technology Development program are to:

1. Define and ascertain instrument needs of potential PIs.

2. Modify a commonly available instrument to make it compact, rugged, power efficient, and microgravity-ready.

3. Make the LLS instrument modular to allow it to be easily reconfigured and optimized for a wide range of experiments which await the forthcoming Microgravity Fluids NASA Research Announcement (NRA or AO).

4. Automate and enhance data taking and analysis for the modular LLS instrument.

5. Collect data sets on the traditional state-of-the-art, room-size instrument in our laboratory for evaluation of the hardware and software under development and to further develop in-house expertise in preparing and analyzing different classes of samples.

6. Test miniature LLS modules attached to fiber optic probes with protein crystal growth experiments in collaboration with Professor Wm. Wilson of Mississippi State University / MSFC.

7. Simulate vibration and low-gravity performance.

8. Test back-scatter fiber optic probes.

9. Acquire and evaluate a simultaneous multiangle LLS instrument.

10. Provide assistance to the STDCE (Surface Tension Driven Convection Experiment) flight hardware project when it is in need of LLS diagnostics. While not a specific objective of the work, since we have the capability we have taken on this other program of interest of MSAD.

APPROACH

NASA Lewis Research Center is providing and coordinating the technology for placing a compact Laser Light Scattering instrument in a microgravity environment. This will be accomplished by defining and assessing user requirements for microgravity experiments, coordinating needed technological developments and filling technical gaps. This effort is striving to brassboard and evaluate a miniature multiangle LLS instrument. We expect to see this ATD effort become a flight hardware development project once NASA's Microgravity Fluids AO is released and the many LLS proposals we have solicited are then submitted in response to NASA Headquarters. FY90 funding supports one of the two Lewis people on the project and has forced a freeze in the developments supported by grants and in some of the hardware advances. We do believe that the reader will still be impressed with what follows.

PROGRESS (Elaborates Program Objectives)

1. NASA Lewis held an Advanced Technology Development (ATD) Laser Light Scattering Workshop in September of 1988. Major LLS contributors, manufacturers, and potential PIs from around the world attended the workshop. Many issues were settled in formal and informal discussions during the two day workshop. A draft version of the Workshop Proceedings was edited and issued soon after the workshop and a final, 308 page version of the Workshop Proceedings (NASA CP-10033) was published August 1989.

In January of 1990 another meeting of potential LLS PIs took place in Washington DC. At this meeting, more than a dozen researchers discussed and shared their ideas and proposal outlines.

We exhibited the back scatter fiber optic probes discussed below at the Microgravity Fluids workshop in mid 1990. This gave us a chance to discuss the LLS project with additional potential PIs and to excite the LLS community with a live demonstration of technology that is on the cutting edge.

The forthcoming Microgravity Fluids Announcement of Opportunity (December 1990) contains a section for laser light scattering which will solicit not only proposals for microgravity LLS experiments, but additional PI instrument parameters and details of how the PIs plans to store samples and initiate experiments (e.g. - chemically, thermally, through photopolymerization, etc.).

2. Dr. Robert G.W. Brown has served as a hardware consultant to this project. He invented and has patented many of the advances needed for making the miniature modules and improving the detectors used in LLS. He has provided detailed lists of the necessary miniature module specifications and ways of insuring these specifications have been met. The core of these specifications are provided for the reader in Appendix 1. At the January Washington DC meeting, Dr. Brown, associated with Royal Signals and Radar Establishment (RSRE), showed RSRE developments in miniature LLS systems in a presentation to potential PIs. Some of these systems had been designed specifically for NASA needs, and they are about a year ahead of the rest of the world. This meeting gave potential PIs a chance to look ahead at what is technologically possible and it gave NASA and RSRE important feedback on how well the needs of the potential PIs are being met.

3. Single angle detector and laser modules have been breadboarded, but have yet to be finished and delivered to the LLS laboratory at NASA Lewis for evaluation. This delay is the result of a reorganization of Defense Technology Enterprises (DTE), which was the commercial arm of RSRE. The Laser Dynamics group of DTE has since broken off and formed their own company (in alliance with a large parent company) and should be able to deliver the modules before the year is out. We intend to check the miniature instrumentation by repeating measurements which are difficult to make with traditional LLS instrumentation. Details follow in section 5.

4. The maximum likelihood correlator algorithms being developed by Professor Robert Edwards of Case Western Reserve University (CWRU) for this project are in their second year of development. The analysis portion of the prototype software for extracting particle size distributions, errors, and goodness of fit from single angle Quasi Elastic Light Scattering (QELS) data and later automating the LLS instrument is nearly completed and early results are very promising. The prototype code was written in APL, which allowed it to be rapidly modified. However, the APL code now needs to be translated to a language that can be compiled to give rapid results. The code is in the process of being documented and one of our next programming tasks at the LLS laboratory at NASA Lewis will be recoding this program using a fast compiled language. This portion of the project is on a no cost extension while we await funding for its completion. The addition of multiangle algorithms will give more information and promises to decrease the stiffness of the numerical problem and make it easier to fit histograms to the data sets. The development of the multiangle code by Professor Cheung at the University of Akron, in collaboration with Professor Edwards, is

going well, and is now consistently extracting bimodal and trimodal particle size distributions from the data libraries discussed in the next section. Professor Cheung's work is also on a no cost extension since the ATD project was only funded for one of its two Lewis scientists (the other's salary was provided by the MMSL at NASA Lewis) and hence could not offer continued support for its grant research.

The core of correlator control program for single detector input is now finished and is being used at Lewis to automatically take data, analyze it, and print out the results. The analysis algorithms are being enhanced at Lewis with additional Mie algorithms. These allow the experimenter to account for scattering asymmetries that arise with samples larger than 1/10 the wavelength of the incoming light. Two out of three Mie routines planned for the enhancements are now coded and running. The automatic LLS instrument parameter setup routines provided by the maximum likelihood algorithms remain to be added to the correlator program.

5. LLS experiments conducted in our laboratory have given us many data sets for analysis and testing of both the software and hardware being developed for this ATD effort. While this library of data is needed for evaluating the modular miniaturized hardware in its different configurations, it also perfects in-house expertise in challenging LLS experiment areas. An eight page listing of ATD LLS experiments prior to March of 1990 was previously submitted to Stuart Glazer at NASA Headquarters. We have attached several tables giving an overview of our more recent dynamic LLS work with single, bimodal, trimodal, and multimodal distributions made in-house from standards. Additional work in static light scattering on polymeric systems is provided Zimm/Berry plots and has been included in Appendix 2. These data libraries have been and will continue to be essential for evaluating both our multiangle algorithm developments and the miniature LLS modules when they arrive.

6. Our collaboration with Professor Wm. W. Wilson (MSFC) has been on hold while we await the arrival of our miniature LLS modules. We have kept in touch and have shared some recent experimental published work from the Journal of Crystal Growth with Professor Wilson discussing the detection of nucleation in protein crystals using LLS.

7. An electronic vibration isolation system with seismic control (a next generation EVIS design from Newport) has been installed and is ready to test the miniature single angle LLS modules when they are delivered.

8. Significant advances in back-scatter fiber optic probes have resulted from a grant initiated by this LLS ATD project with Professor Dhadwal at SUNY-Stony Brook. These fiber optic probes will allow LLS to be used in a solution that does not allow a laser beam to pass through it. Their larger viewing volume may prove to be of great importance when LLS is applied to protein crystal growth experiments. While waiting for the LLS modules to arrive, we have invested significant amounts of research time characterizing the revolutionary fiber probes. Tables summarizing some of the hundreds of data sets taken in this study are included in Appendix 3. With the back scatter probes, we have been able to study milky concentrations ranging up to 10% weight concentration without multiple scattering problems. These probes will be useful for both protein crystals and, in another form, for fractal studies. Multiple angle and low angle probes will be developed when funding allows.

9. Evaluation of the miniature modular multiangle LLS unit will begin when it is received. It can hopefully be purchased with 1991 funding. Note that the currently planned level of funding is sufficient only to cover salaries of the two Lewis investigators. Additional funds are required for the purchase of brassboard items. It will be used to study polydispersity, cross-correlation, and dynamic depolarized light scattering (DDLS). This brassboard of optics and simultaneous detectors will allow testing of our multiangle software with simultaneous multiangle scattering on samples that change too quickly to be evaluated with currently available equipment.

10. We have run hundreds of LLS tests on samples of particles (alumina, glass microspheres, pliolyte) proposed for use by the STDCE project. Two particle size distributions are illustrated in Appendix 4. We have presented them with written reports outlining our findings. These studies showed aggregation problems and a background of fine residual (dust) particles which destroy the background contrast for the cameras. After finding the problem, we identified a possible solution. Professor John Ugelstad in Norway supplied us with 70% porosity particles which are nearly density matched when they fill with the solution they are placed into. They are also all spherically symmetric and monodisperse (ie. - identical in size). Professor Ugelstad is willing to make and sell 90% porosity particles. This information has been passed to the STDCE project.

KEY PERSONNEL

William Meyer - NASA/LeRC via CWRU contract
Project Manager
* overall management of the ATD effort
* reporting to NASA Headquarters
* submitting progress reports to NASA/LeRC
* Progress Items 1-4, 9

Dr. Rafat Ansari
Research Scientist - NASA/Lewis via CWRU contract
* Progress Items 5-10

CONCERNING THE APPENDICES WHICH FOLLOW

The following appendices are provided to show individuals knowledgeable in the field of LLS the kind of data analysis presently available for this project. While enhancements are being added, the software available to and developed by this project is quite advanced. The data presented in the following appendices is presented prior to publication and we ask that it be cited accordingly by the reader.

APPENDIX 1

SUMMARY OF DR. R.G.W. BROWN'S 26 PAGE REPORT CONCERNING THE SPECIFICATION OF AVALANCHE PHOTODIODE DETECTORS FOR USE IN STATIC AND DYNAMIC LIGHT SCATTERING

PARAMETER	VALUE	PROOF/DOCUMENTATION
Pulse height distribution	Clean, unimodal	Graph/Plot
Dark count Rate	<300 cts/sec PCS <1000 cts/sec LDV	Value @ Operating Temperature
Dead Time	<50nsec (<20ns if possible)	Pulse picture
Count rate stability	<+/- 1/2% over experimental time	Graph/plot over over 30 minutes
Temperature stability	<+/- 1/50 °C	Plot of constant source
Voltage stability (bias)	<+/-2 or 3 mV	Plot of constant source
Quantum efficiency	>25% SLIK (if available) >7.5% C30921S	State method of proof
Linearity of count rate	up to 10 MHz at rate	Graph
Afterpulsing	<0.04%	Calculations +9
Factorial moments	up to 3rd or 4th	Calculations for n>2
Power consumption	depends on cooling typically less than 6 Watts	Result of measurement
Operational temperature range	Constant ct rate over T	Graph/Plot
Anti-lock up after saturation		
Output pulses	Compatible with chosen correlator	

SUMMARY OF DR. R.G.W. BROWN'S 20 PAGE REPORT CONCERNING THE SPECIFICATION OF SEMICONDUCTOR LASER DIODES FOR USE IN STATIC AND DYNAMIC LIGHT SCATTERING

PARAMETER	VALUE	PROOF/DOCUMENTATION
Mode structure	TEM_{00}	Data sheet/far field photograph
Mode hopping	Zero after warm-up	Graph/plot over 30 minutes
Wavelength	780 or 850 nm typically	Monochromator output
Output power	>20mW over 30 minutes	Graph of plot over 30 minutes
Factorial Moments	Up to 3rd or 4th +/- error	Calculations for n>2
Excess correlations	<0.04%	Results of Auto-measurements at 20K and 100K cts/sec
Coherence length/ linewidth	>3m / <80MHz	Manufactures data sheet or Spectrum-analyzer plot
Laser beam diameter/ collimation	as chosen	Photo, Ronchi test or knife edge convolution
Polarization	500:1 if possible +/- 1/10° alignment	Alignment accuracy fading plot
Power consumption	depends on cooling	Result of measurement
Operational temperature range	Constancy over T	Graph/Plot
Temperature stability	+/-0.5 °C	Graph/Plot
Voltage stabilities	+/-2 or 3mV	Plot of constancy

APPENDIX 2

(GLOSSARY)

This glossary is provided with the assumption that the reader has some knowledge of LLS. Many volumes have been written on the terms listed below. We are providing this glossary to insure that the abbreviations in the following tables are meaningful.

1. **Conc.**: Weight/volume solids concentration in percent.

2. **Diff.Coeff.**: Diffusion coefficient. The rate at which a particle diffuses is strongly dependent upon this parameter. In simpler terms, the driving force results from a gradient in concentration which causes particles to move from regions of high concentration to regions of low concentration.

3. **2dCum**: Second cumulant of a fourth order cumulant analysis. This analysis describes the size distribution of the particles by its moments. Information on the shape of the distribution function is not provided by this method.

4. **PDP**: Polydispersity parameter of the system being studied.

5. **DblExp**: Double exponential. A double exponential often fits data quite well, but not much can be inferred unless additional evidence of a bimodal model exists.

6. **ExpSam**: Exponential sampling is also known as Pike-Ostrowski analysis. This technique does not assume a fixed number of modes.

7. **NNLS**: A non-negatively constrained least squares algorithm described by C.L. Lawsen and R.J. Hansen in "Solving Least Squares Problems", Prentice-Hall, 1974.

8. **Contin**: Contin is capable of analyzing a variety of related numerical problems for the regularized solution of linear algebraic and linear Fredholm integral equations of the first kind. It contains options for peak constraints and linear equality and inequality constraints. It was developed by S.W. Provencher in the Federal Republic of Germany.

9. **RMS ERROR**: Root-mean-square error from residual plots as a function of correlator channel.

10. **CNTRT**: Total number of photons counted in one second.

11. **GAMMA**: Half-width at half-maximum of the intensity fluctuation spectra due to Brownian motion of particles. The diffusion coefficient is extracted from Gamma.

12. **% ERROR** indicates % error in Gamma, and hence in diffusion coefficient measurement.

13. **Radius of gyration** is defined as the square root of the weight average of all the mass elements.

14. **2nd Virial Coeff.** provides a measure of particles interactions in the system being studied.

TABLE 1

LASER-LIGHT SCATTERING STUDIES OF MONODISPERSE SYSTEMS
(SPHERICALLY SYMMETRICAL IDENTICAL PARTICLES)

Angle degrees	Diff.Coeff. Cm^2Sec^{-1}	DIAMETER IN NANOMETERS 2dCum	PDP	DblExp	ExpSam	NNLS	Contin	BEST FIT	RMS ERROR	CNTRT KHz	GAMMA rad/s	% ERROR
(DOW 91 nm)												
15	4.83E-8	92.9	0.15	N/A	159	82	101	NNLS	2.25E-3	485	95.5	1.00
20	4.58E-8	90.5	0.24	88	117	90	75	2dCum	7.23E-4	356	173.3	0.32
30	5.19E-8	91.0	0.07	89	79	85	N/A	NNLS	4.26E-4	288	384.1	0.29
45	5.60E-8	85.1	0.05	N/A	68	83	101	Contin	5.68E-4	164	896	0.33
60	5.73E-8	85.0	0.01	N/A	85	84	101	ExpSam	4.15E-4	218	1530	0.27
90	5.62E-8	87.2	0.002	N/A	88	86	N/A	2dCum	6.22E-4	134	2983	0.42
120	5.45E-8	89.6	0.008	N/A	90	87	N/A	2dCum	5.70E-4	171	4356	0.34
135	5.43E-8	88.7	0.03	N/A	88	90	101	2dCum	3.69E-4	198	5009	0.22
150	5.32E-8	87.1	0.09	N/A	144	83	N/A	NNLS	1.92E-4	262	5571	0.85
160	5.26E-8	89.4	0.07	87	90	84	92	ExpSam	2.25E-4	344	5645	0.17
(DOW 482 nm)												
30	1.06E-8	466.4	0.005	N/A	472	461	N/A	2dCum	1.31E-4	2155	466.4	0.19
60	7.34E-9	627.7	0.11	690	404	571	N/A	NNLS	5.94E-4	88.7	627.8	0.86
90	9.68E-9	486.3	0.07	484	769	499	486	2dCum	5.01E-4	57.5	535	0.31
135	3.10E-9	1087	0.45	952	1583	786	1938	NNLS	7.45E-4	26.9	408	1.34
(DOW 1.082 micron)												
30	3.77E-9	1364	0.005	N/A	1122	1277	N/A	2dCum	9.07E-4	649	25.5	0.84
45	3.69E-9	1244	0.14	1188	1132	1026	1328	Contin	5.03E-4	136	61.3	0.53
60	3.22E-9	1387	0.20	1101	762	1097	1620	DblExp	8.23E-4	48.6	93.8	1.17
90	3.20E-9	1194	0.28	1241	1269	872	1008	NNLS	7.88E-4	30	218	0.71

Parameters: Temperature: 25°C; Laser Wavelength: 514.5 nm; Particles: Polystyrene polymer.

TABLE 2

LASER-LIGHT SCATTERING STUDIES OF POLYDISPERSE SYSTEMS
(MIXTURES OF DIFFERENT SIZE PARTICLES)

Angle degrees	Diff.Coeff. Cm^2Sec^{-1}	DIAMETER IN NANOMETERS 2dCum	PDP	DblExp	ExpSam	NNLS	Contin	BEST FIT	RMS ERROR	CNTRT KHz	GAMMA rad/s	% ERROR
BIMODAL (CWRU 39 nm and DOW 91 nm)												
30	7.62E-8	56.1	0.20	55	50	49	71	Contin	2.03E-4	335	622	0.40
60	7.86E-8	55.6	0.17	53	51	52	70	ExpSam	3.92E-4	186	2341	0.39
90	8.07E-8	53.7	0.17	55	66	47	54	Contin	4.64E-4	157	4849	0.24
135	7.98E-8	54.4	0.18	54	53	50	54	Contin	4.39E-4	212	8161	0.32
160	7.89E-8	54.2	0.20	54	85	53	78	DblExp	2.68E-4	408	9314	0.17
TRIMODAL (CWRU 39 nm, DOW 91 nm and 482 nm)												
20	1.06E-8	394	0.36	313	215	290	523	DblExp	3.52E-4	2665	39.9	1.32
30	1.00E-8	396	0.36	325	461	314	499	NNLS	1.02E-4	1563	87.9	1.29
30	1.01E-8	391	0.29	328	215	245	518	Contin	5.42E-4	1604	89.0	1.40
60	4.36E-8	82.9	0.27	78	78	69	171	NNLS	3.33E-4	138	1568	1.14
90	4.00E-8	88.8	0.28	84	77	70	167	Contin	3.66E-4	114	2929	1.08
135	5.72E-8	70.0	0.22	70	71	59	136	NNLS	6.58E-4	130	6345	0.55
150	3.16E-8	94.0	0.35	85	85	52	62	NNLS	4.22E-4	216	5165	1.49
MULTIMODAL (CWRU 39 nm, DOW 91 nm, DOW 482 nm and DOW 1080 nm)												
30	0.70E-8	551	0.36	439	557	431	882	NNLS	2.31E-4	1492	63.2	1.52
60	1.90E-8	141	0.48	116	72	59	172	NNLS	3.10E-4	129	925	2.10
90	2.42E-8	125	0.28	96	91	46	261	NNLS	6.37E-4	90	2083	3.15
135	2.55E-8	106	0.27	89	81	62	134	NNLS	4.96E-4	102	4187	2.85
150	1.23E-8	173	0.40	111	148	61	410	Contin	3.32E-4	170	2802	4.59

Parameters: Temperature: 25°C; Laser Wavelength: 514.5 nm; Particles: Polystyrene polymer.

APPENDIX 3

FIBER OPTIC LIGHT SCATTERING RESULTS

TABLE 3: 35 NM (Lot # 1900223A)

PARAMETERS:

Particle Standard: Bangs Polystyrene 35 nm.
Wavelength=632.8 nm, T=20°C, Angle=157°
Run time: 5 minutes

Conc. %	Diff.Coeff. Cm^2Sec^{-1}	DIAMETER IN NANOMETERS 2dCum	PDP	DblExp	ExpSam	NNLS	Contin	BEST FIT	RMS ERROR	CNTRT KHz	GAMMA rad/s	% ERROR
0.01	9.99E-8	42.1	0.03	N/A	42	42	N/A	2dCum	9.91E-4	16	6858	0.72
0.05	10.6E-8	39.2	0.06	39	49	38	40	2dCum	2.84E-4	72	7362	0.17
0.10	10.7E-8	39.3	0.04	N/A	39	37	41	2dCum	3.51E-4	53	7342	0.22
0.50	11.1E-8	37.8	0.04	N/A	37	35	40	ExpSam	1.40E-4	343	7633	0.05
1.00	11.4E-8	36.6	0.05	37	37	37	38	NNLS	6.73E-5	300	7888	0.03
2.50	11.8E-8	35.4	0.05	35	35	35	36	NNLS	8.18E-5	665	8146	0.07
5.00	12.2E-8	33.8	0.07	33	34	19	N/A	DblExp	6.81E-5	615	8544	0.26
10.0	12.0E-8	33.6	0.09	34	33	33	35	ExpSam	2.62E-4	177	8575	0.14

REMARKS: All measurements were taken using a Neutral Density Filter of OD.40

FIBER OPTIC LIGHT SCATTERING RESULTS

TABLE 4: 85 NM (Lot # 1900214A)

PARAMETERS:

Particle Standard: Bangs Polystyrene 85 nm.
Wavelength=632.8 nm, T=20°C, Angle=157°
Run time: 5 minutes

Conc. %	Diff.Coeff. Cm^2Sec^{-1}	DIAMETER IN NANOMETERS 2dCum	PDP	DblExp	ExpSam	NNLS	Contin	BEST FIT	RMS ERROR	CNTRT KHz	GAMMA rad/s	% ERROR
0.01	4.77E-8	87.3	0.052	N/A	81	86	101	2dCum	3.73E-4	38.01	3304.5	0.23
0.05	4.87E-8	86.4	0.035	N/A	86	82	N/A	2dCum	6.66E-4	17.66	3338.9	0.44
0.05	4.95E-8	86.2	0.008	N/A	87	84	N/A	2dCum	3.58E-4	132.3	3343.8	0.25
0.10	5.12E-8	82.3	0.031	N/A	82	81	N/A	2dCum	2.84E-4	155.4	3502.9	0.22
0.10	5.10E-8	84.4	0.005	N/A	N/A	81	N/A	2dCum	1.49E-4	253.0	3415.9	0.10
0.20	5.16E-8	83.5	0.005	N/A	84	80	N/A	ExpSam	2.87E-4	436.3	3451.8	0.25
0.25	5.30E-8	80.0	0.020	N/A	80	78	N/A	ExpSam	4.04E-4	624.2	3604.0	0.38
0.30	5.20E-8	81.3	0.025	N/A	81	81	N/A	ExpSam	2.24E-4	537.2	3547.0	0.09
0.40	5.31E-8	79.9	0.018	N/A	80	78	N/A	ExpSam	5.76E-4	694.8	3609.4	0.23
0.50	5.39E-8	77.1	0.054	N/A	71	74	76	2dCum	2.64E-4	974.8	3741.3	0.26
0.60	5.43E-8	76.9	0.048	N/A	71	75	N/A	2dCum	1.96E-4	792.4	3751.9	0.18
0.70	5.38E-8	77.0	0.059	N/A	77	75	N/A	2dCum	1.80E-4	912.0	3745.6	0.18
0.80	5.51E-8	75.0	0.062	N/A	106	72	N/A	2dCum	2.71E-4	949.2	3845.0	0.27
0.90	5.48E-8	75.4	0.061	76	95	74	76	Contin	4.45E-4	990.7	3822.5	0.18
1.00	5.71E-8	73.2	0.045	N/A	71	73	76	ExpSam	5.39E-4	1360	3939.9	0.34
5.00	6.25E-8	64.6	0.099	61	41	51	73	NNLS	9.72E-5	983.2	4464.0	0.51

REMARKS: All measurements were taken using a Neutral Density Filter of OD.40

FIBER OPTIC LIGHT SCATTERING RESULTS

TABLE 5: 165 NM (Lot # 1890620C)

PARAMETERS:

Particle Standard: Bangs Polystyrene 165 nm.
Wavelength=632.8 nm, T=20°C, Angle=157°
Run time: 5 minutes

Conc.	Diff.Coeff.	DIAMETER IN NANOMETERS						BEST	RMS	CNTRT	GAMMA	%
%	Cm^2Sec^{-1}	2dCum	PDP	DblExp	ExpSam	NNLS	Contin	FIT	ERROR	KHz	rad/s	ERROR
0.005	2.70E-8	161.3	0.005	N/A	163	151	N/A	2dCum	3.95E-4	128	1788	0.12
0.01	2.67E-8	161.3	0.005	N/A	163	153	N/A	2dCum	3.45E-4	200	1788	0.13
0.05	2.77E-8	157.7	0.005	N/A	134	144	N/A	2dCum	8.22E-4	578	1828	0.22
0.10	2.75E-8	151.8	0.048	N/A	140	145	179	2dCum	5.20E-4	811	1900	0.26
0.20	2.78E-8	147.9	0.070	144	148	N/A	106	ExpSam	1.81E-4	1098	1950	0.11
0.30	2.84E-8	147.3	0.043	N/A	143	145	N/A	ExpSam	5.86E-4	984	1958	0.31
0.40	2.82E-8	145.4	0.075	144	140	138	130	ExpSam	2.02E-4	984	1984	0.13
0.50	2.84E-8	143.8	0.083	144	199	142	N/A	2dCum	4.97E-4	883	2006	0.28
0.60	2.85E-8	143.0	0.083	143	141	95	N/A	NNLS	3.05E-4	749	2017	0.30
0.70	2.88E-8	140.7	0.095	153	129	106	N/A	ExpSam	7.65E-4	666	2049	0.58
0.80	2.98E-8	133.6	0.11	133	115	89	150	NNLS	2.01E-4	651	2158	0.49
0.90	3.15E-8	121.7	0.16	131	113	49	136	Contin	4.48E-4	516	2370	0.82
1.00	3.21E-8	117.3	0.18	102	85	98	158	ExpSam	1.05E-3	536	2458	1.00
2.50	10.6E-8	32.80	0.15	36	35	21	32	NNLS	1.63E-4	300	8779	2.54
2.50	14.1E-8	22.30	0.30	19	17	12	44	NNLS	1.98E-4	339	12958	2.10

REMARKS: All measurements were taken using a Neutral Density Filter of OD.40

FIBER OPTIC LIGHT SCATTERING RESULTS

TABLE 6: 261 NM (Lot # 1B73 SERAGEN)

PARAMETERS:

Particle Standard: Seragen Polystyrene 261 nm.
Wavelength=632.8 nm, T=20°C, Angle=157°
Run time: 5 minutes

Conc. %	Diff.Coeff. Cm^2Sec^{-1}	DIAMETER IN NANOMETERS 2dCum	PDP	DblExp	ExpSam	NNLS	Contin	BEST FIT	RMS ERROR	CNTRT KHz	GAMMA rad/s	% ERROR
0.005	1.63E-8	260.1	0.017	N/A	260	258	267*	2dCum	6.76E-4	N/A	1108	0.23
0.01	1.65E-8	260.8	0.005	N/A	264	257	259*	2dCum	2.54E-4	N/A	1105	0.19
0.05	1.68E-8	255.2	0.005	N/A	258	251	256*	2dCum	1.68E-4	N/A	1130	0.13
0.10	1.67E-8	257.4	0.005	N/A	260	250	250*	2dCum	3.35E-4	N/A	1120	0.28
0.20	1.78E-8	233.0	0.06	224	234	217	245	Contin	3.63E-4	195	1238	0.23
0.30	1.71E-8	230.0	0.13	239	236	201	240	NNLS	2.48E-4	229	1255	0.30
0.40	1.72E-8	223.0	0.16	225	200	197	206	NNLS	3.04E-4	295	1293	0.39
0.50	1.83E-8	203.4	0.182	210	188	156	341	NNLS	4.94E-4	228	1418	0.59
1.00	1.03E-8	226.0	0.179	205	195	186	303	NNLS	3.60E-3	309	1457	0.78

REMARKS: * represents Contin calculations without Mie corrections in the limit 200,400 nm.

AIAA 91-0779
A Preview of a Microgravity Laser Light Scattering Instrument

William V. Meyer and Rafat R. Ansari
NASA Lewis Research Center / CWRU
Cleveland, OH

29th Aerospace Sciences Meeting
January 7-10, 1991/Reno, Nevada

A PREVIEW OF A MICROGRAVITY LASER LIGHT SCATTERING INSTRUMENT

W. V. Meyer and R. R. Ansari
NASA Lewis Research Center/CWRU, Cleveland, Ohio 44135

Abstract

Laser Light Scattering offers a non-invasive optical technique for rapidly acquiring a wealth of information about particles in suspension. Examples of the instrument's usefulness in microgravity are given, and the building blocks from which one can assemble instruments for a multitude of experiments are described.

This paper is written for both a general audience and an audience familiar with the technique of laser light scattering. With this in mind, technical details are delayed until a brief general introduction has been given. The Reference section lists some classic texts in the field (1 - 12).

Introduction

NASA Lewis Research Center is developing and coordinating the development of a versatile, miniature, modular light scattering instrument for use in microgravity. Laser Light Scattering (LLS) will be used to measure microscopic particles in the size range of thirty angstroms to above three microns. It is a non-invasive technique which can determine particle structure, weight-average molecular weight and particle-particle interactions.

Everyone is familiar with the effects of light scattering from seeing the colorful glow of a sunrise or sunset. In the laboratory, light scattering is used to study a range of phenomena, many of which are adversely affected by gravity. Nucleation, spinodal decomposition, gelation, critical phenomena, aggregation, diffusion, etc. are influenced by gravity and can be better studied in a microgravity environment with LLS. LLS may also be an important enhancement for protein crystal growth experiments, which need quantitative information about the growth process and an indication of the onset of nucleation. Table 1 highlights some of the uses for laser light scattering in a low-gravity environment. The main reason for considering microgravity in these studies is to attain freedom from convective flows caused by gravity. Many of the structures to be studied are delicate; some would be damaged by the motion of Stokes settling.

LLS works by passing a laser beam into a sample and illuminating suspended particles in the process. The light scattered from thousands of these particles is collected at different angles, and the signal from the detector is analyzed.

There are several ways to perform laser light scattering. Classical or static light scattering uses the average intensity of the light at different angles in the scattering plane for making calculations. It is an important tool for determining particle structure, weight-average molecular weight and particle interactions (see Table 1). As used in this paper, dynamic light scattering is a digital technique which monitors the changes in the average intensity of the scattered radiation caused by the Brownian motion of the particles. A digital correlator analyzes the signal, and with proper models we can then obtain the average particle diffusion coefficient, which in turn gives average particle size and size distributions. Particle sizes from three nanometers to above three microns can be determined. Dynamic depolarized laser light scattering is different from regular dynamic light scattering in that it examines the horizontally polarized scattered light coming from the sample. This weak, depolarized signal contains dynamic and structural information which is not otherwise readily available.

The use of solid-state and semiconductor lasers, the possibility of placing avalanche photodiode detectors simultaneously at multiple angles, miniature correlators, fiber optics, and advanced algorithms promise a versatile, modular, miniature instrument with enhanced capabilities. The modular approach will allow the LLS instrument to be easily reconfigured and optimized for a wide range of experiments. For example, the laser, detector, and correlator modules can be attached to either several individual fiber optic backscatter probes or to a single multiangle module. Multiangle analysis routines will improve polydispersity measurements and give higher resolution size determinations.

The modular approach will allow implementation of different kinds of light scattering: dynamic and static light scattering, dynamic depolarized laser light scattering, number fluctuation spectroscopy, electrophoretic light scattering and surface light scattering. This allows us to be flexible in meeting the needs of microgravity scientists.

According to current plans, the first modules to be assembled will be defined by the needs of investigators selected through a NASA Announcement of Opportunity (AO) for microgravity fluids research. The Laser Light Scattering section of NASA's AO is soliciting proposals for microgravity laser light scattering experiments and the instrument parameters needed by the Principal Investigator along with related plans for storing samples and initiating experiments (e.g. chemically, thermally, by photopolymerization, etc.). To assist the potential experimenter in specifying instrument parameters, the laser light scattering modules' capabilities are listed below. The building blocks for constructing LLS instruments include:

<u>LLS Modules</u>

1. Light Sources and Signal Detection
2. Receiving Optics
   a. Simultaneous multiangle arrays
   b. Fiber optic probes
3. Signal Processing
   a. Maximum likelihood algorithms
   b. Polydispersity algorithms

<u>Light Sources and Signal Detection</u>

Robert G. W. Brown, of the Royal Signals and Radar Establishment (RSRE) and Sharp Laboratories of Europe, has served as a hardware consultant to this project. He has pioneered many of the advances needed for making miniature LLS modules and improving the detector circuits used in LLS (13-18). He has provided NASA with extensive specifications for miniature laser and detector modules and details for ensuring these specifications have been met. This section on light sources and signal detection draws upon his work.

Compact laser diode modules (approximately 2.5 x 1 x 1 inches) with a power consumption of less than one Watt now exist. They are available for a number of wavelengths. The specifications which follow apply to the 780 nm wavelength diode laser. This wavelength is significant because it is the shortest visible wavelength available from laser diodes which have more than 20mW of power. The modules use laser diodes operating in a continuous wave (CW) mode and exhibiting a single longitudinal mode and a TEM_{00} transverse mode. They have powers greater than 20 milliwatts and their power stabilities vary less than 1% RMS over 30 minutes. They have a 500:1 polarization, coherence lengths greater than 3.75 meters, laser linewidths less than 80 MHz, a beam size of about 1.5 mm in diameter, and they exhibit less than 0.04% excess autocorrelations. The laser element lifetime exceeds 10,000 hours.

The compact Avalanche Photo Diode (APD) modules (approx. 4 x 1 x 1 inches) can each contain two detectors. Unless otherwise noted, the following specifications assume active quenching circuits and SLIK (super low k) detectors for the APD modules. The detectors are Peltier cooled and have a nearly constant dark count which is less than 300 counts per second (cps) with single stage cooling and less than 30 cps with double stage cooling. Their quantum efficiencies are greater than 35-40% at 780nm, and their afterpulsing is less than 0.04% on time scales greater than 50 ns. Their dead time is less than 20 ns, (200 ns with passive quench circuits) and their count rates can exceed 20 MegaCts (2 MegaCts with passive quench circuits) with a stability that varies less than +/- 1/2% for thirty minutes. The detector element lifetime exceeds 10,000 hours and the modules self-reset after saturation.

Receiving Optics

a. One possible experimental configuration consists of a simultaneous multiangle detector array with detectors placed at approximately five degree intervals beginning near zero degrees and extending close to 180 degrees. By using two laser sources, we essentially double the number of detector angles and at the same time achieve reliability though redundancy. This can be achieved by using two lasers of the same frequency entering the scattering cell at different angles or by using two lasers of different frequencies entering the scattering cell through a dichroic mirror. This configuration will allow the use of interchangeable sample cells which can be individually temperature controlled. When the light from the laser enters a traditional sample cell, the cell must be surrounded by an index matching fluid to avoid reflection caused by the change in index of refraction from air to glass. This reflection, commonly referred to as flare, interferes with the signal from the sample. Studies requiring a high signal to flare ratio may use a special scattering cell or a set of receiving optics, under development. If successful, these options will achieve acceptable performance without the need for an index matching fluid.

b. Newly developed fiber optic probes (19-21) can be used for both static and dynamic light scattering measurements, and they will allow flexibility for a number of experiments. These backscatter fiber optic probes have been developed by Harbans Dhadwal at SUNY Stony Brook with partial support from the NASA LLS project. They have been tested in our laboratory over a wide range of concentrations. Typically, current LLS technology can address only dilute suspensions (suspensions which do not exhibit multiple scattering or particle-particle interactions), but with the backscatter probes we have been able to accurately measure standards of 30 nm particles with weight concentrations as high as 10% solids (milky white) without the need for an index matching fluid. With 161 nm particles we have been able to measure weight concentrations as high as 0.5% without the multiple scattering problems encountered in conventional LLS instruments. Results from our studies with the backscatter fiber probes are being prepared for publication. It is anticipated that these probes will be useful for both protein crystals and, in their low angle multiple probe form, for fractal studies. The multiple angle and low angle probes are still in the development and testing stage.

Signal Processing

Algorithms which will increase the

resolution of dynamic light scattering and automate the instrumentation are under development at Case Western Reserve University (CWRU), The University of Akron, and NASA Lewis Research Center.

Maximum likelihood parameter estimation expressions for the measurement variance will be available to examine the effect of various time lag schemes of the correlator. The residual errors that result from various measurements are examined and with this information, the maximum likelihood algorithms determine which experimental parameters need to be changed in order to optimize speed, accuracy and goodness of fit. This provides a quantitative estimation of how well an experiment will proceed, assuming a given number and spacing of angles, correlator delay setting, correlator channel spacing, etc. Robert V. Edwards is performing this work at CWRU.

Multiangle fit algorithms which can constrain the parameters of the particle size distribution, and thereby give better polydispersity measurements and higher resolution, are also under development by H. Michael Cheung at Akron. They eliminate the angular bias introduced by the relative scattering efficiencies of different size particles when using Mie scattering functions. These algorithms are presently working using APL and are being recoded using a fast compiled computer language.

The core of the correlator control program for single detector input is being used at Lewis to automatically take data, store it, analyze it, and print the results. The analysis routines are being enhanced at Lewis with additional Mie algorithms. They allow the experimenter to account for scattering asymmetries which arise with particles larger than one tenth the wavelength of the incoming light.

In addition to the software developments described above, NASA Lewis is using an enhanced version of the LLS analysis software available from Brookhaven Instruments Corporation (BIC) in Holtsville, NY. Lewis has modified the original source code and has the permission of BIC to use it for both its Advanced Technology Development project and for flight hardware. The enhanced versions of this computer code, along with others being developed for this project, will be available for Principal Investigators working with NASA. This analysis package includes:

1. A fourth order cumulant analysis. This analysis describes the size distribution of the particles by their moments. Information on the shape of the distribution function is not provided by this method.

2. A double exponential analysis. This fits data sets which contain two size distributions. However, without additional evidence that two sizes of particles exist, its results are inconclusive.

3. Exponential sampling analysis, also known as Pike-Ostrowski analysis. This technique does not assume a fixed number of particle size distributions, making it more general than a double exponential analysis.

4. A non-negatively constrained least squares algorithm, which is described in reference 22.

5. Contin, an analysis program capable of analyzing a variety of related numerical problems for the regularized solution of linear algebraic and linear Fredholm integral equations of the first kind. It contains options for peak constraints and linear equality and inequality constraints. It was developed by S.W. Provencher in

the Federal Republic of Germany.

The LLS modules, once configured, can be tested with a library of test data generated from standards at NASA Lewis. This will help ensure that each LLS instrument assembled from the above optical building blocks is fully functional.

Conclusion

As we have seen, a LLS instrument built from modules allows several configurations, each optimized for a particular experiment. While a multiangle LLS instrument will probably be mounted in a rack in the space shuttle and on Space Station Freedom, other configurations are both possible and likely. It is possible that a space shuttle glove-box and a lap-top computer containing a correlator card can be used to perform a number of experiments and to demonstrate the technology needed for more elaborate investigations. This offers a simple means of flying a great number of experiments without the additional requirements of full-scale flight hardware experiments. Glove-box experiments are taken up as stowage and thus provide experimenters with an easy path to microgravity.

The NASA Lewis LLS team is looking forward to working with Principal Investigators to develop a flight instrument which will enable a number of flight experiments, add valuable diagnostics to others, and advance ground based studies requiring laser light scattering. For more information, please feel free to contact William Meyer or Rafat Ansari at NASA LeRC, M.S. 105-1, 21000 Brookpark Road, Cleveland, OH 44135. Our respective phone numbers are (216) 433-5011 and (216) 433-5008.

The authors acknowledge the support of the Microgravity Science and Applications Division, Code SN, of NASA.

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TABLE 1. Laser Light Scattering Instrument
Capabilities for Microgravity Research and Applications

AREAS OF STUDY	MODE	PROCESSES/PARAMETERS
Aggregation	DLS/Static	Fractal dimensions
Bacterial Suspensions	DLS/DDLS	Suspension dynamics
bacteriophage		Rotational effects
E. Coli		Helical motions
spermatozoa		Swimming speed distributions/motility
Clays	DLS/Static	Rates of coagulation
Colloidal Crystals	DLS	Size distribution
ceramic superconductors		
Colloidal Dispersions	DLS	Diffusion coefficient
		Size distribution
		Interparticle interactions
Electrophoresis	ELS	Mobilities/Zeta potential
Controlled Drug Delivery	DLS/Probes	Diffusion coefficient
Diagnostic Tool	All of the above	Desired properties:
urine characterization		identify proteins
blood characterization		aggregation/shape
detection of cataracts		aggregation of lipids
water quality monitoring		identify sub-micron particles and bacteria
Emulsion Polymerization	DLS	Particle growth monitoring
		uniform size particles
Environment Control	DLS	Recovery of fine particles
flocculation		polymer-polymer interactions
		electrostatic interactions
Gels	DLS	Network interaction
Highly Interacting Systems	Backscatter	Hard-sphere interactions
Microemulsions	DLS/Static	Microemulsion structure
Milk/Curd products	Backscatter	Particle size distribution
Novel Structures	DDLS	Shapes (e.g. rods/ellipsoids)
minerals		size distribution
DNA/RNA		coil dynamics
microtubules		rod dynamics
vesicles		flexing/Size distribution
on-line process monitoring	Probes	desired transport properties
Polymer and Macromolecules	Static/DLS	Shape, size and conformation
long-chain polymers		internal motions/flexing
blood plasma		aggregation
synthetic insulin		molecular properties
Protein Crystallization	Probes	Onset of nucleation
Viruses TMV, TRV	DLS/DDLS	Trans/rotational motions

GLOSSARY

Backscatter: Fiber optic probes employed in a backscatter configuration
DLS: Dynamic Light Scattering
DDLS: Dynamic Depolarized Light Scattering
ELS: Electrophoretic Light Scattering
Static: Total intensity measurement
Probes: Fiber optic probes