A BRIEF REPORT
SOFT CONDENSED MATTER

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1. An overview

Here, I shall breifly summarize the contents of this report which includes all that I have done and learnt in this short stay at IGCAR.

- What are Colloids?
- Dynamic Light scattering(DLS) and measurement of Particle Diameter(size disribution)
- Measuring Volume Fraction of a Colloidal suspensions
- Colloidal Crystals and the properties of Colloidal suspensions in Gas-like, liquid-like and Crystalline ordering by Static Light Scattering

IGCAR and CMI.

2. What are Colloids?

Colloids or Colloidal Suspesions are mesoscopic systems[1]. They are composite systems consisting of Fluid and Dispersed Particles of size much larger than the molecules in the fluid. They are usually in the range of $10nm$ to $1\mu m$. The upper limit ensures that Brownian motion of the colloidal particles is not dominated by gravity. We will be studying monodisperse spherical particles with a very small size distribution. These systems infact under suitable conditions have gas-like, liquid-like, glass-like and crystal-like ordering.

They have a close relation in Elastic constants E which is approximately Un_p, where U is the interpartice interaction energy and n_p is the particle concentration, with the atomic solids (with just some scaling). For example, U is almost same for both, and say n_p in a colloid suspension is about $10^{13}cm^{-3}$,then E is appx. $10dynes/cm^2$ and in a conventional atomic crystal of $n_p = 10^{23}$ has E around $10^10dynes/cm^2$. This is also seen in other properties like latent heat of melting, etc. As, the dimension of the colloidal particle is three orders larger than the atomic crystal, the time scales for diffusion are also scaled appropriately, hence, making the time scale of colloid particle motion to range from microseconds to seconds which is accessible to the methods of Dynamic Light Scattering which is the one that I ahve used for the following results that I obtained. Due to this fact, the various things about the atomic crystals can be learnt on colloids crystals, which now serve as models.

We have two different types of Colloidal systems, namely, Lyophilic[2] and Lyophobic[3]. The Lyophobic are of interest to me, because the suspension that I have used is **KSS Latex**, which falls in this category. These have to be stabilized to prevent agglomerations(i.e a jumbled mass). This stabilization is done in two ways,

(1) Charge Stabilization: By electric charge on the surface resulting in electrostatic repulsion between particles.
(2) Steric Stabilization: By adsorption of large molecules of particles.

Here, I shall try to brief upon the theory behind the Dynamic and Static Light Scattering because we use Dynamic Light Scattering in

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[1] They are the intermediates between Macroscopic and Microscopic systems

[2] These are thermodynamically stable.

[3] They require extra energy for their formation and because of the large free energy between the particles and the solvent.

getting the particle size Distribution and hence helping in the measurement of the average diameter as well as the Polydispersity of the Colloid Dispersions. The Static Light Scattering is helpful in measuring the Form Factor of the Colloid and hence in recognizing the phase i.e Gas-like, Liquid-like or Crystal like.

3. Dynamic Light Scattering(DLS) and the measurement of Particle Diameter

The experimental setup that is used consists of a Ar-Kr laser, the goniometer where we place the light scattering cell which contains the sample nad a detector which is connected to the PC which acts as a correlator. The wavelength of the Laser that I have used during my experiment is $514.5nm$. The laser is cooled by an external cooler which pumps cool water into the casing around the emitting part. We focus the laser beam onto the sample with the help of an in-built lens. The scattering angle at which we prefr to measure for measuring particle diameter is usually kept large for the partciles of sizes around $100nm$ so that the scattering volume is kept optimal.

If we go to smaller scattering angles, the scattering volume becomes larger and hence, we might have some not so good readings due to dust particles staying for a longer time. I measured at 90^o and 120^o. We can the set the temperature of the sample and the angle at which to measure through the computer itself. We check for the counts and optimize them to around 70-100 per second, so that the intensity is not very large. Then, we take the readings and the program calculates the Partice size with polydispersity. If the Poly dispersity is beyond 17

Few precautions that I learnt in handling this setup:

- We need to switch on the cooler before we switch on the laser and allow it to start pumping the cold water, otherwise the laser will have a very bad damage, because there might be heating of all the elements inside the Laser due to high amount of dissipated power.
- We must allow the laser to stabilise before we switch the detector on and begin to take readings, because we will not get proper results.
- We have to first focus our primary part of laser that come out after scattering, so that the beam passes through the center of the sample.

- We must never allow detector to come in direct contact with the primary beam of laser, because this will damage the PMT that is present inside.

DLS has become a very powerful method in getting the size distrbution of small particles in medium. The measurement of time dependence of the scattered light at a particular angle is analyzed by calculating the normalized internsity autocorrelation function, $g^{(2)}$, from which the field correlation function, $g^{(1)}$, be evaluated by Siegert Relation. This 1 is related to the Dynamic Structure Factor, also called the Intermediate Scattering Function,**F(Q,t)**. All the mathematical relations are given below.

$$g^{(2)}(Q,t) = \frac{\langle I_s(Q,t) I_x(Q,0)\rangle}{\langle I_s(Q,0)\rangle^2} \tag{1}$$

whereI_s is the Intensity. The denominator is the square of average intensity.

$$g^{(1)}(Q,t) = \frac{\langle E_s^*(\vec{Q},0) E_s(\vec{Q},t)\rangle}{\langle E_s(\vec{Q},0)\rangle^2} \tag{2}$$

where E_s is the electric field. Now, the relation between $g^{(1)}$ and F(Q,t) is given by

$$g^{(1)}(Q,t) = \frac{F(\vec{Q},t)}{S(Q)} \tag{3}$$

where

$$F(\vec{Q},t) = \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}\langle \exp(\iota\vec{Q}.\{\vec{R}_i(0) - \vec{R}_j(t)\})\rangle \tag{4}$$

For a large number of Scatters, we assume, $E_s(\vec{Q},t)$ to be a Gaussian Random Variable,hence getting,

$$g^{(2)}(Q,t) = 1 + \delta \mod g^{(1)}(Q,t)^2 \tag{5}$$

where δ is dependant on geometry of the experiment.

For measuring the particle size distribution the sample prepared is very dilute, so that multiple scattering can be avoided. Usually, we make it so that the liquid in the light scattering cell is not turbid. The results of my experiment can be seen in PLATE I. We can see in the graph of Intensity that the percentage in class is way below 20, hence we can conclude that KSS Latex will crystallize. In fact, the KSS Latex sample that I was using itself has irridisence, which tells that it has crystals at that concentration.

This is how the program calculates the Diameter of the particle. It measure $g^{(2)}$ at say 90^o and hence we can also get $g^{(1)}$. For a non-interacting suspension, we expect $g^{(1)}$ to have a single exponential form. Hence on doing the same fit as $g^{(1)}(Q,t) = c\exp(-\Gamma t)$ where $\Gamma = D_0 Q^2$, c is a constant and D_0 is the Diffusion Coeeficient of Einstein-Stokes relation $D_0 = k_B T/6\pi a\eta$, k_B, the Boltzmann's Constant,η is the dynamic viscosity,and a, the radius of particles. Hence, we can calcuate the diameter of the paricle.

4. Measurement of Volume Fraction

Volume fraction is measured for a colloidal suspension so as to make samples of the suspension with varying known volume fraction to crystallize them and then do light scattering on the known volume fraction samples.

For this calcuation, we initially take a small quantity, say $200\mu l$ of the suspension, about three to four in number in small cups made out of alluminium foil. Before this the weight of the foil cups are measured and noted and similarily , we measure along with the suspension. Then, we let the sample to dry till all the water in the sample evaporates and only the dry particles are left. Then we again take the weight of this.From this, we can calculate the weight of the dried suspension alone. We take the average of the weights and from this this the volume fraction can be calualted as follows

$$\phi = \frac{\langle W_{dry} \rangle}{(volume)(\rho_{water})}$$

From which we can calculate the particle concentration $n_p = \frac{6\phi}{\pi d^6}$.

Wt. of Al foil alone	0.0369 g	0.0349 g	0.0350 g
Wt. of Al foil with $200\mu l$ of suspension	0.3032 g	0.2980 g	0.2990 g
Wt. of Al foil with dried suspension	0.0485 g	0.0443 g	0.0455 g
Wt. of Dry Suspension alone	0.0116 g	0.0129 g	0.0105 g

5. Colloidal Crystals and the properties of Colloidal suspensions in Gas-like, Liquid-like and Crystal-like ordering by Static Light Scattering

5.1. **A Brief review of Static Light Scattering.** Static Light Scattering is a technique used for colloid suspensions in whihc we measure the Intensity of the scattered light from the sample mounteed in a similar setup to the DLS, but now we take the measurements at various angles. This is generally used for getting the plot of $S(Q)$ vs. Q and generally gives information about the ordering of the particles in the suspension at the given volume fraction. Measurements can be made to find diameter, etc. for the particles. For crystals, from the intensity plot we can get the Bragg Spot which can be used in recognizing the crstal structure, i.e BCC, FCC, etc.

The samples for Crystal-like and Liquid-like ordering are taken with volume fractions of 0.005/0.0029 and 0.0025 along with sufficient resins in plastic vials and are shaken thoroughly. The crystal one is shaken till we can see some irridisence in the vial wehn it is left for sometime. The samples are then transferred to quartz light scattering cells which contain resins are are left to stay still so as not to disturb their ordering.

We measure th intensity I_s of the scattered light at various angles and the plot is taken. We know that the scattered electric field is $\vec{E_s}(\vec{Q},t) = \sum_{i=1}^{N}\sum_{\alpha_i=1}^{N} A \exp \iota \vec{Q}.$, where r_{i,α_i} is the position vector of the scattering center α_i in the ith particle at time t and can be written as the sum of the center of mass position $R_i(t)$ of particle i and the position vector $S_{\alpha_i}(t)$ of the scattering center. Hence we can get I_s from this. We also know that the Scattering wave vector is

$$\vec{Q} = \frac{4\pi\mu_m}{\lambda}\sin(\theta/2)$$

where μ_m is the refractive index of the medium, λ is the wavelength of the laser and θ is the scattering angle.

We can show that he time averaged intensity in the Rayleigh approximation is $I_s(Q) = CP(Q)S(Q)$ where $S(Q)$ is the structure factor and$P(Q)$ is the Form Factor. We know that the Form factor for a spherical particle of radius a is

$$P(Q) = 9\frac{\sin(Qa) - Qa\cos(Qa)}{(Qa)^3}^2$$

We can get exprimentally $S(Q)$vs.Q plot also.

5.2. **Gas-Like Ordering.** For this we take a very dilute sample of the suspension, approximately, $\phi = 0.0001$ and we cary out the Static Light scattering on it from an angle of 20^o to 150^o in steps of 5^o. We expect the Intensity to be independent of Q because in a sample of so low volume fraction we expect the particles to be almost non-interacting. infact the graph of $S(Q)$vs.Q that we observe (given in PLATE II) is almost constant.

5.3. **Liquid-like ordering.** In this I made the KSS latex suspension to be having $\phi = 0.0025$. The suspension is placed along with Ion-exchange resins for removal of ions that are present. From this, I took a sample of $0.75ml$ in a light scattering cell along with which are placed resins to a few mm height and shaken thoroughly till we can see the irridiscence. Then we do the static Light scattering on the sample and we get the resulting graph of $S(Q)$ vs. Q after correcting for form factor. From the graph we can calculate the Q_{max}. After getting this, we can calculate the n_p as

$$n_p = \frac{1}{\sqrt{2}}\{\frac{Q_{max}}{2\pi}\}^3$$

from which we get the experimental value of ϕ by the familiar formula. All the details about this are listed out in PLATE III.

5.4. **Crystalline Order.** For this, my sample which has $\phi = 0.005$ was not useful, because it was too turbid and this method does not give proper results for such cases. So, I have taken a previous sample, which has $\phi = 0.0029$ and did the SLS on this. I got the first Bragg Peak at $\theta = 45^o$ and then with the help of a paper and a pen located various others brighter spots in the range of the outlet. The $S(Q)$ vs. Q graph shows the peak, we can also see the other peaks faintly. This sudden peaking shows that the ordering in the sample is crystalline.

BCC plane	BCC expected ratio	experimental ratio	FCC Expected ratio	FCC plane
110	1	1	1	111
-	-	-	1.154	200
200	1.414	1.34	-	-
211	1.732	1.66	1.633	220
201	2	1.92	1.915	311
310	2.236	2.17	2	222
222	2.449	2.39	2.309	400

From this we can see that, the values are close to BCC than FCC for the sample. Hence, we can conclude that the crystal structure for the sample is BCC.

REFERNCES:

(1) THe thesis of Mr. Mohanty was very helpful.
(2) Dynamic Light Scattering by Pecora
(3) Wikipedia
(4) Also, few papers by Dr. B.V.R.Tata was helpful in learning few facts whihc I might o might not have used in this report.

Acknowledgements:
I would initially like to thank Dr. N. Subramaniyam and Dr. Sundar for making this program instrumental, CMI and IGCAR for this programme. I would like to thank Dr. B.V.R.Tata for taking me into his lab for learning. I would also like to thank Ms. Brijitta for helping me in doing the experiments.

AUTOSIZER

Size Report

KSS Latex
100 micron aperture
Laser Power 20 mW, With filter #1

Sample

Record Number:	2
Filename:	100507.sz2
File Path:	G:\RAVICM~1
Sample RI:	1.60, Abs:0.00
Dispersant RI:	1.33
Disp. Viscosity (cP):	0.890
Date (DMY):	10/05/07
Time:	11:44:50

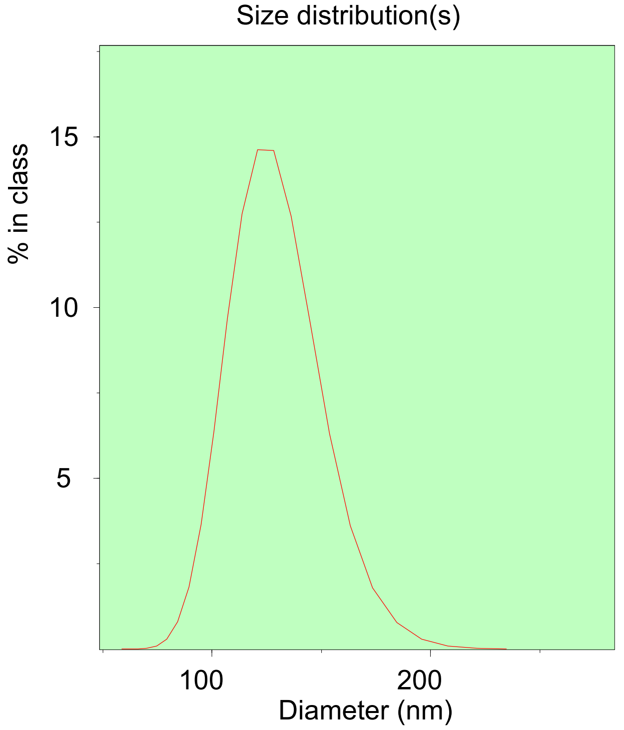
System

Instrument Type:	Autosizer 4700
Temperature (°C):	25.0
Count rate (kCps):	79.9
Cell Type:	ZET5110
Detector Angle (deg.):	90.00
Wavelength (nm):	514.5

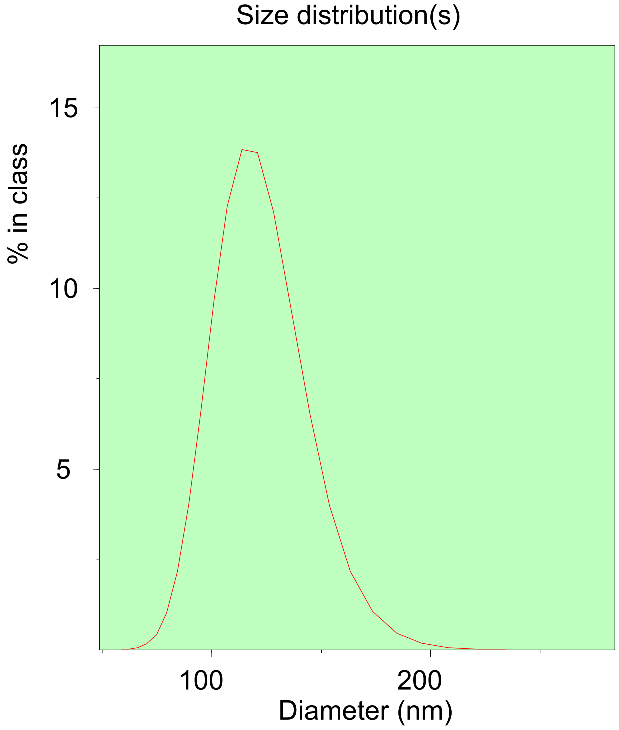
Result

Quality Factor:	Pass
Z Average Mean(nm):	124.5
Polydispersity:	0.03
Intensity Mean (nm):	126.1
Volume Mean (nm):	119.0
Analysis Mode:	Auto:Cumulants

Intensity



Volume



Size(nm)	Intensity	Volume	Number
58.6	0.0	0.0	0.0
62.2	0.0	0.0	0.1
66.1	0.0	0.0	0.2
70.2	0.0	0.2	0.6
74.6	0.1	0.4	1.3
79.2	0.3	1.0	2.7
84.1	0.8	2.2	4.9
89.4	1.8	4.0	7.7
94.9	3.7	6.6	10.7
100.8	6.4	9.6	13.1
107.1	9.7	12.3	14.1
113.8	12.7	13.8	13.4
120.9	14.6	13.8	11.3
128.4	14.6	12.1	8.4
136.4	12.7	9.4	5.5
144.9	9.6	6.5	3.2
153.9	6.3	4.0	1.6
163.5	3.6	2.2	0.8
173.6	1.8	1.1	0.3
184.4	0.8	0.5	0.1
195.9	0.3	0.2	0.0
208.1	0.1	0.1	0.0
221.1	0.0	0.0	0.0
234.8	0.0	0.0	0.0

Peak Analysis by intensity

Peak	Area	Mean	Width
1	100.0	126.1	48.5

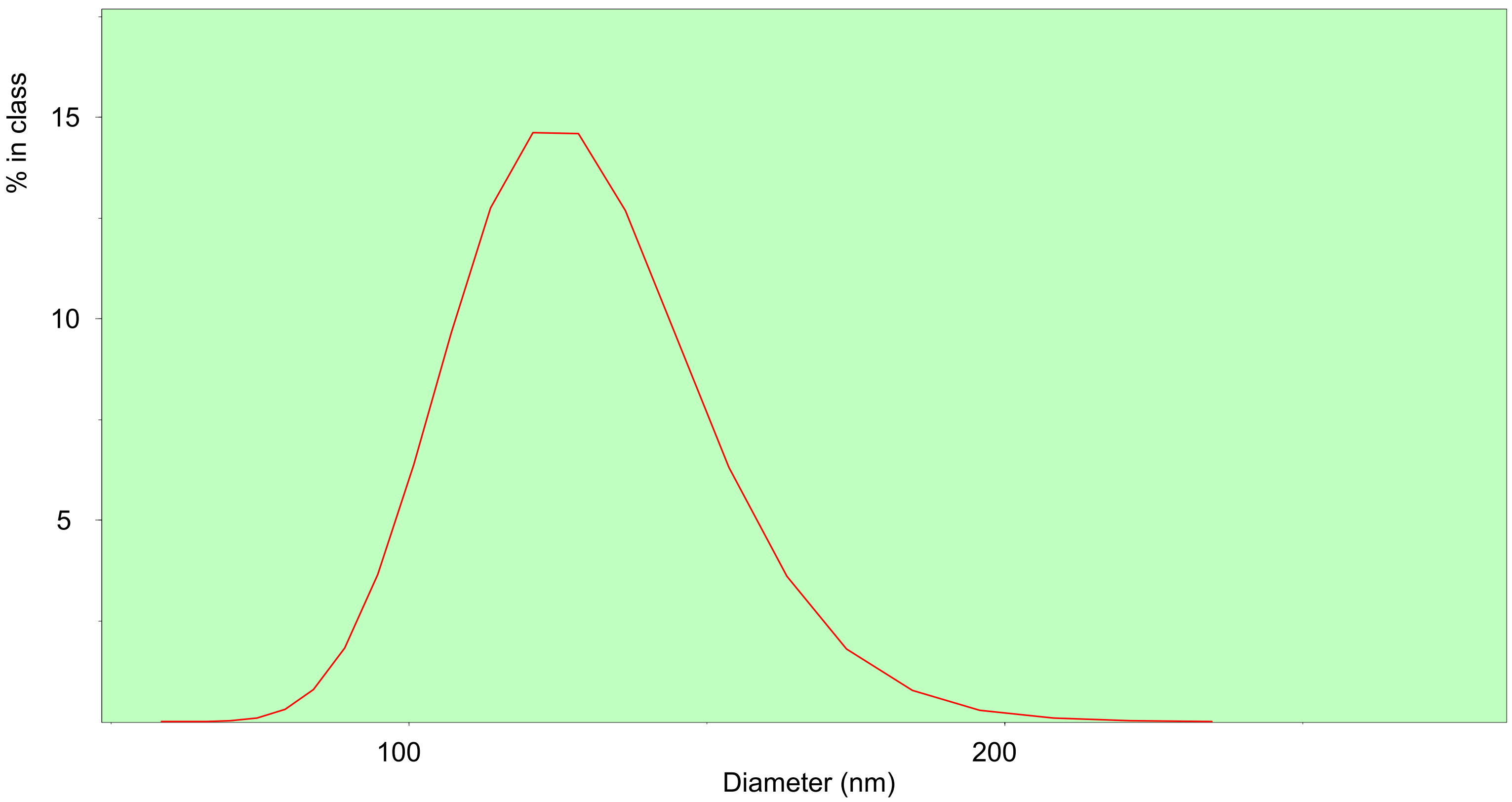
Peak Analysis by volume

Peak	Area	Mean	Width
1	100.0	119.0	48.2

Peak Analysis by number

Peak	Area	Mean	Width
1	100.0	109.5	43.9

Size distribution(s)



Rec	Angle	KCounts	ZAve(nm)	Poly.Index	Quality	Error	In Range	Merit	Analysis	Title
2	90.0	79.9	124.5	0.0262	Pass	3.89e-004	97.3	72.6	Auto:Cumulants	KSS Late