

Course Number 001-2-0029
 Final Assessment
 March 2, 2017

SOLUTIONS/DISCUSSION IN GREEN

BASICS

- 1) List any 3 properties of suspended materials that we can measure using LS.

Any of the following: radius of gyration, hydrodynamic radius, molecular weight (for polymers and proteins), fractal dimension, second virial coefficient, critical micelle concentration, form factor, structure factor, shape factor.

- 2) What are the units of q ? Why is it more physically significant to discuss q -dependence than to discuss angular dependence?

The scattering vector q has units of inverse length, and is more physically significant than angle, as it signifies the "length scale of investigation" for structure studies using static light scattering. Static light scattering can provide different information for suspended materials with sizes larger than q as compared to materials sized smaller than q . This phenomenon is illustrated particularly well when considering $I(q)$ to investigate aggregate fractal dimension or the form and structure factors of a sample. In other words, q provides a physically meaningful way to non-dimensionalize R , the size of the particles being measured.

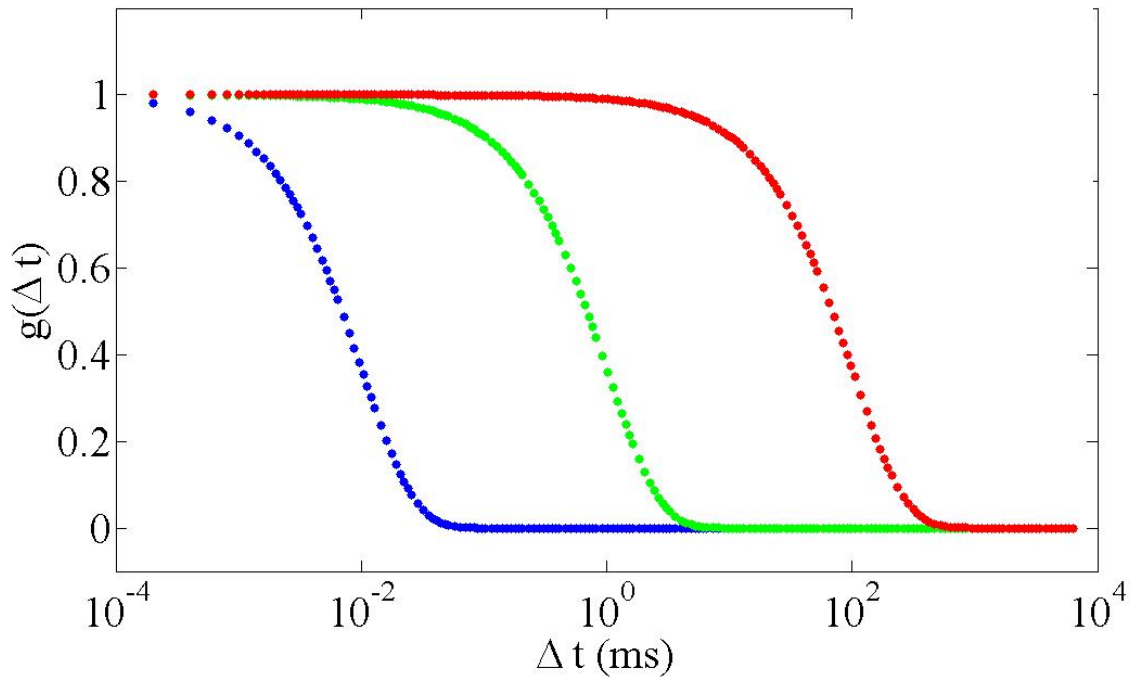
- 3) Match the terms on the left with the appropriate symbol, description, or equation on the right.

Items are rearranged to be in the appropriate order:

Scattering vector	$(4\pi n \sin(\theta/2)) / \lambda$
Radius of gyration	$\Sigma m_i r_i^2 / \Sigma m_i$
Hydrodynamic radius	Size as measured by DLS
Fractal dimension	Indication of aggregate shape/structure
Correlation function	DLS raw data
Index of refraction	n , a measure of light bending in a material
Shape factor	R_g/R_H

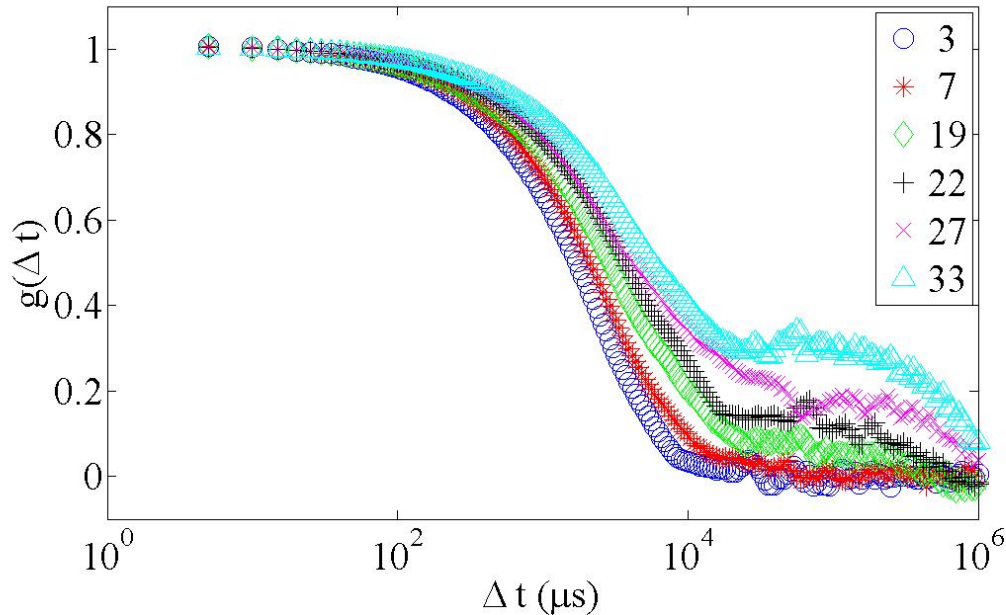
DYNAMIC LIGHT SCATTERING

- 4) In the plot below, label the data indicating the largest and smallest particles in suspensions. How do you know?



The correlation function g exhibits an exponential decay. The meaning of the exponential decay time is the diffusive time scale of the particles in suspension as they diffuse in and out of the cross section of the incident light. The diffusive time scale is directly related to the particle size: small particles diffuse faster while larger particles diffuse more slowly. The blue curve exhibits the shortest diffusive time scale and thus has been produced by the smallest sized particles, while the red curve exhibits the longest or slowest diffusive time scale and thus has been produced by the largest sized particles.

Questions 5-7: You are measuring the growth of particles over time in sample X. You find raw data that looks like the following, at times as given in the legend:



- 5) About how many populations of particles are there at the start of the measurement?

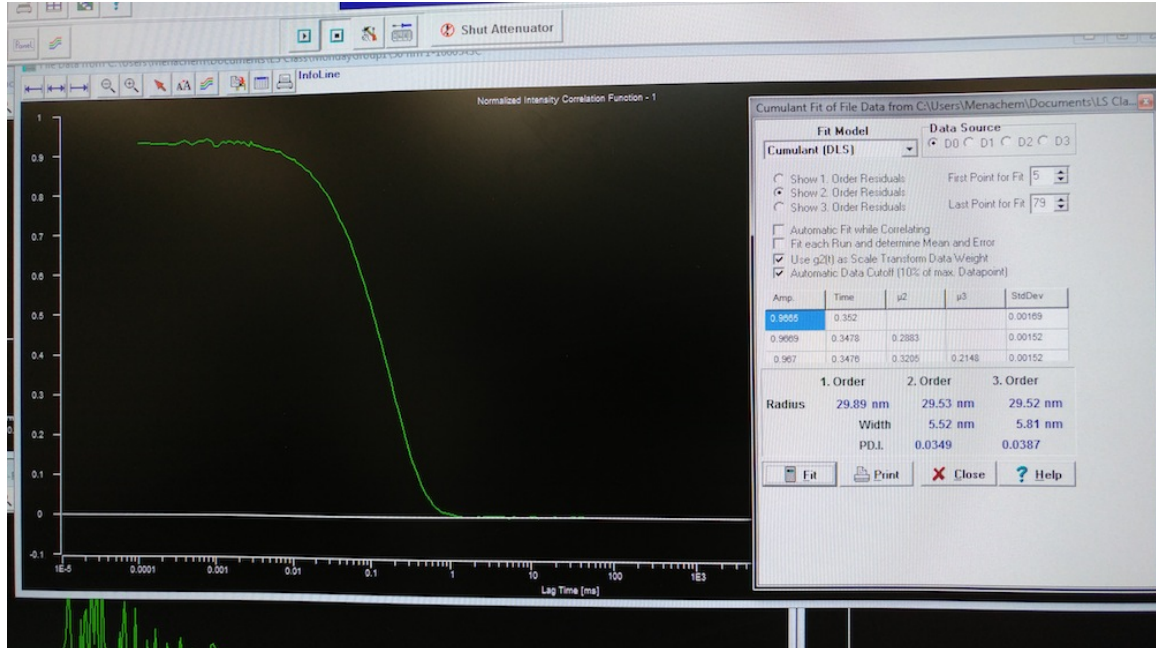
Based on the shape of the curve at 3 (minutes), shown by the blue open circles, there appears to be a single exponential decay and therefore a single population of particles.

- 6) About how many populations of particles are there at the end of the measurement?

Based on the shape of the curve at 33 (minutes), shown by the light blue open triangles, there appear to be two distinct decays, indicating two distinct particle populations, one much larger (by ~2 orders of magnitude) than the other.

- 7) Which of the following fit methods is most appropriate for assessing the particle growth in this case?
- Cumulant
 - CONTIN/Regularized**
 - Single exponential
 - Linear fit on a log-log scale

- 8) Below is an example correlation curve and “simple fit,” i.e. cumulant fit, from the Day 1 measurements of the particle standards. The table below reproduces the numbers from the “simple fit” window. Given both the correlation curve and the results of the fit, is the cumulant fit an appropriate method to obtain particle size from this data set? Why or why not?



	1. Order	2. Order	3. Order
Radius	29.89	29.53	29.52
Width		5.52	5.81
PDI		0.0349	0.0387

The raw data correlation function seen in the plot appears to have a single decay. It is reasonable to begin with a “simple fit” cumulant analysis. When we do this, we see that: 1) the 1st, 2nd, and 3rd order results for the particle radius agree with each other quite well, within 1%, and that 2) the values for the PDI, or polydispersity index, are between 0.03 and 0.04, indicating very monodisperse particles. Had the PDI values been larger than ~0.3, we may want to try alternative fits. A third way to evaluate the cumulant fit to the raw data is to observe the residuals of the fit, which are not shown in the image above, but which are displayed in the plot in the lower left quadrant of the software window. In summary, **YES** it is reasonable to obtain particle size via the cumulant analysis in this particular sample.

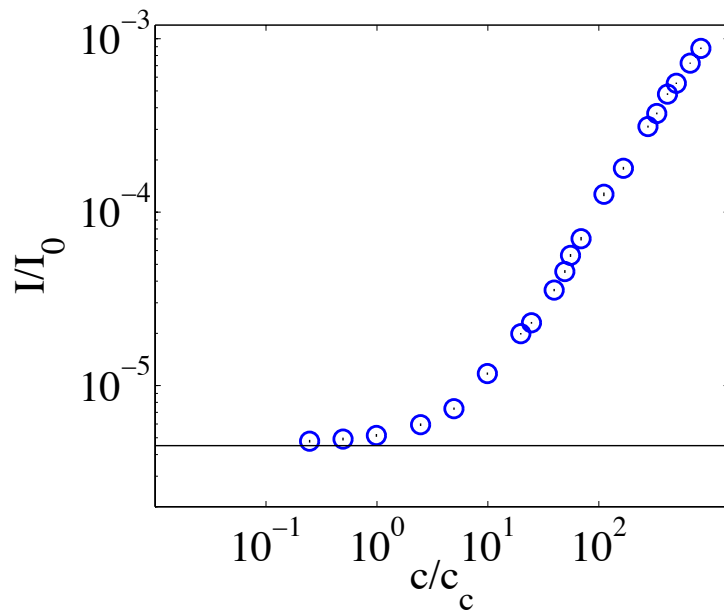
- 9) Your advisor gives you a mystery sample to measure. It is dark, somewhat turbid, and you cannot tell by eye if there are precipitates or visible aggregates in suspension. Discuss 2 possible ways you might prepare the sample for light scattering, and what measurement would you want to do? Describe your reasoning.

There are many different ways to approach this problem. For light scattering characterization in particular, samples must be not too turbid in order to provide reasonable measurements. So, we must either dilute and/or filter the sample before measuring, so that it is no longer too turbid for light to pass through. Furthermore, if we are unsure of the presence of large aggregates, we may consider sonication to break up these aggregates before measuring the sample. After initial size measurements at 90 degrees, we may consider doing SLS measurements

CMC MEASUREMENTS

10) Our cmc measurements on Day 2 did not immediately give us a cmc result for the surfactants we measured. We measured intensity as a function of concentration. What were we expecting to see in the plot of intensity vs. concentration? Draw the shape of the expected curve of I vs. c .

We were expecting to see behavior like the plot shown here. The solid line indicates the amount of scattering from the solvent alone. There is little to no additional scattering from solutions at low concentrations. However, at larger concentrations, the intensity as a function of concentration begins to increase. This change in slope of intensity as a function of concentration indicates the phase transition from single surfactant molecules to micelles, known as the cmc.



11) Discuss some possibilities for why our first run of surfactant samples did not immediately yield good results for the cmc, and what you would do next if you wanted to measure the cmc more accurately.

To measure the cmc more accurately, multiple samples should be prepared throughout the desired concentration range, to confirm sample-to-sample reproducibility in the intensity data. Extra care should be taken to use clean solvents and sample vials, especially for very low concentrations of surfactant.

GRAPHENE OXIDE MEASUREMENTS

12) Does the graphene oxide sample which we measured in the Anton Paar zeta potential instrument have a well-defined PZC? Yes or no, and why?

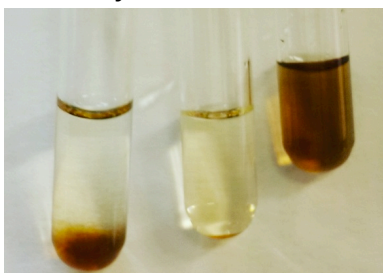
No, the graphene oxide sample measured using the Anton Paar instrument did not have a well-defined PZC: all samples measured in the range of pH 1 to 10 were negatively charged. We did not observe any polarity change (sign change) of the zeta potential despite the wide range of pH measured, and so we did not find the PZC, or the pH at which the particles are uncharged and the zeta potential is 0.

13) Plot average size vs. pH for the samples prepared at 1.1, 3.2, 7.4, and 9.6. Also plot zeta potential as a function of pH. **ANSWERED IN SPREADSHEET**

14) Discuss/explain the trend of size vs. pH in light of the zeta potential results.

Larger magnitudes of the zeta potential indicate greater stability of particles in suspension. The magnitude of the zeta potential is lowest in the particles with pH 1. Hence, we expect these particles to be the least stable in suspension, and to exhibit aggregation. The highest pH investigated, nearly 10, exhibited the largest magnitude zeta potential, near -50 mV, indicating very stable particles. Even before measuring particle size, we expect these particles to be the smallest measured. Indeed, both samples at pH 1 and pH 3 contained particles which had already aggregated, while the suspension prepared at pH 10 contained the smallest and most stable particles.

15) The image shows 3 of the graphene oxide samples, at pH 1.1, 3.2, and 9.6. Guess which is which. How do you know?



Given the measurements of particle size and the discussion in number 14 above, it appears that the sample on the left is at pH 1.1, as it clearly exhibits settling that occurs when particles aggregate. While the middle sample appears more homogeneous, we can observe a small collection of settled particles at the bottom of the container. While not as unstable as the sample at pH 1.1, the sample in the middle is likely the sample at pH 3.2. On the right we find the sample prepared at pH 9.6: the uniform and deeper color indicates more stably dispersed particles throughout the sample, without evidence of separation.

STATIC LIGHT SCATTERING

Questions 16-17: choose from the following:

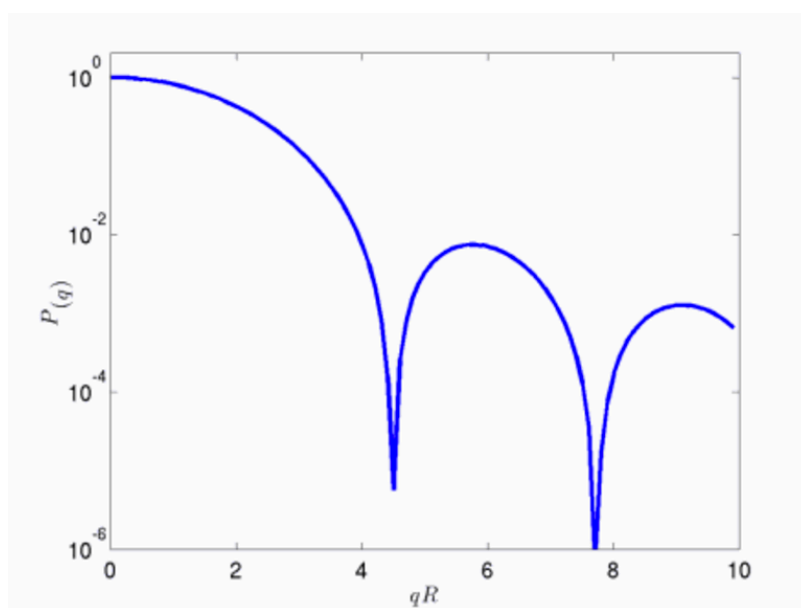
- a) I/I_0 vs. q
 - b) Kc/R vs. q^2
 - c) $G(\Delta t)$ vs. Δt
 - d) I vs. time
 - e) $P(q)$ vs. qR
 - f) Zimm plot
- 16) When measuring dilute solutes in solution by SLS, it makes the most sense to plot which of the above? Choose all that apply.
- a) Kc/R vs. q^2**
 - b) Zimm plot**
- 17) When measuring particles in suspension, or more concentrated polymers or agglomerated proteins, by SLS, it makes sense to plot which of the above? Choose all that apply.
- a) I/I_0 vs. q**
 - b) Kc/R vs. q^2 (this may be useful, but is usually not the main objective)**
 - c) $P(q)$ vs. qR**
- 18) The Zimm plot allows us to extrapolate Kc/R to both $q \rightarrow 0$ and $c \rightarrow 0$ to measure which of the following? Choose all that apply.
- a) hydrodynamic radius
 - b) intensity
 - c) radius of gyration**
 - d) molecular weight**
 - e) sedimentation velocity
 - f) second virial coefficient**
- 19) Given the compilation of the SLS data obtained on the 800nm particle standard during class, and the 50 and 200nm samples which were measured outside of class, do the following:
- a) Compute columns O through T. The column labels describe the quantity to compute, including units when appropriate. Use the data given in columns A through N.
 - b) Compile all three data sets onto a single spreadsheet, and plot the form factor $P(q)$ vs. qR for all three samples on a single curve. Is there any overlap between the three samples? Why or why not?

- c) Compare the resultant plot with the plot we saw in class (below), which shows the calculated form factor for spheres. Does it agree well? Discuss the salient features which are observed in both your plot and the predicted curve.

ANSWERED IN SPREADSHEET

- 20) The Guinier approximation, $P(q) \sim 1 - (qR_g)^2/3$, allows us to obtain the radius of gyration, R_g , from a linear fit of $P(q)$ as a function of q^2 . Using the data from the 50nm particles, now plot $P(q)$ as a function of q^2 and extract R_g from a linear fit. Obtain the "shape factor" $p = R_g / R_H$, where R_H is the radius measured at an angle of 90. How close do you get to the expected value for spheres?

ANSWERED IN SPREADSHEET



FINAL THOUGHTS/FEEDBACK (NOT GRADED!!!)

(If you prefer, you can submit your feedback anonymously to Moshe)

Why did you take this course? What were your expectations? Did you gain some confidence using light scattering techniques? Will you use LS in the future for your research? How so? What else would you like to learn about LS in the future? How can this course be improved?