Characterizing Gels with Dynamic Light Scattering

Webinar Q&A Transcript

1 Can you rotate the sample inside the sample holder of the LS Spectrometer? Does the software include features related to non-ergodic DLS?

LS Instruments : the LS Spectrometer can be equipped with a sample goniometer to rotate the sample around its vertical axis, enabling non-ergodic DLS as described in the webinar presentation. This element is controlled directly via the software, LsLab. Slow or fast rotation mode can be selected and the rotation speed can be adjusted if necessary.

2 Is there any sense in talking about free diffusion coefficients in the case of hydrogels?

Dr. Usuelli : In hydrogels, the colloidal units form a 3D network that can store mechanical energy and therefore give elastic properties to the considered material. As the colloidal units are in contact with each other, their motion is hindered by surrounding constraints, and it is no longer possible to talk about a free diffusion coefficient. The concept of “free diffusion coefficient” could apply only to those colloidal units which, eventually, are not part of the network and can freely diffuse in the pores of the considered hydrogel. It has to be noted that the free diffusion of such colloidal units happens only within the timescale needed to explore the full size of the pores; at timescales larger than the mentioned one, the dynamics shift to sub-diffusive (and eventually become diffusive again at larger timescales, if the colloidal units are able to “jump” from one pore to the other, as a function of the connectivity of the network).

3 Is it possible/reliable to follow the gelation of a certain system with DLS, when there is a transition from an ergodic system to non-ergodic?

Dr. Usuelli : When a system is making a transition from ergodic to non-ergodic (e.g. during gelation), there are several factors to be taken into account for performing reliable DLS measurements.

A first point to be considered is whether (during the process) the network-forming units experience changes in their size or morphology. In the case of a positive answer, the scattering pattern associated with intra-particles properties (namely, the form factor, P(q)) changes during the process. In parallel, it might be that new refractive index modulations associated with the formation of a network arise. If those modulations are compatible with the length scales associated with the probed q-vectors, then the scattering pattern associated with inter-particles features (namely, the structure factor, S(q)) can also change.

If, during gelation, either P(q) or S(q) change, the ensemble-averaged scattered intensity at a given q-vector ($\langle I(q,t)\rangle_E$) changes and needs therefore to be measured multiple times during the gelation process.

From a pragmatic perspective, it is useful to introduce the following timescales:

- t_M: time needed to perform a time-averaged DLS measurement of a specific sub-ensemble.
- t_E: time needed to perform an ensemble-averaged DLS measurement (while the sample is either translated or rotated)
- t_G: timescale over which the scattering properties of the sample (P(q), S(q)) evolve because of the process.

If the time needed for performing the desired time-averaged and ensemble-averaged DLS measurements is smaller than the time needed for the system to evolve ($t_M + t_E \ll t_G$), then it is possible to perform reliable measurements. It also must be considered the fact that, when a gel is forming, the translation/rotation needed for performing the ensemble averaged measurements might influence the process: this needs to be checked and optimized for each sample.

Instead, if the timescale of the evolution of the system is compatible or faster to the one needed for performing the time- and ensemble- averaged measurements ($t_M + t_E \sim t_G$ *or* $t_M + t_E \gg t_G$), it is not possible to compute/measure reliably the quantities needed for the non-ergodicity correction. In such a case, it would be probably better

to switch to multi-speckle DLS[1] (which enables a faster ensemble averaging, thanks to the multi-speckle nature of the technique) or to other near-field light scattering techniques (Differential Dynamic Microscopy[2], DDM, Time-Resolved Correlation[3], TCR, or Photon Correlation Imaging[4], PCI).

4 In ageing samples, the non-ergodicity is changing with time. What is the time scale of one complete ensemble scan if we want to follow the kinetics of ageing (aggregation / gelation / etc.)? is it e.g. 10 s, 1 min or 5 min?

Dr. Usuelli : This question is closely related to the one above. For a complete ensemble scan, performed in a time t_E, it is important that the rotation speed allows probing a number of sub-ensembles, which is large enough to extract a robust value of $\langle I(q,t)\rangle_E$. Two protocols, for this to happen, can be followed:

- Considering the characteristic time-scale of the evolution of the sample t_G, an ensemble-average time t_E smaller than t_G can be defined. In the considered time t_E, it is possible to compute the robustness of the extracted value of $\langle I(q,t)\rangle_E$ as a function of the rotation speed. Care must be paid to the fact that, if the rotation speed exceeds a threshold value, it might be that the rotation itself affects the properties of the measured sample, or that the sampling-time of the software/instrument does not allow to extract information on the different, measured speckles.
- A value of the rotation speed, which is compatible with the system and instrument of interest, can be defined. Afterwards, the ensemble-average time t_E can be increased, until a plateau in the extracted valued of $\langle I(q,t)\rangle_E$ is seen (in other words, $\langle I(q,t)\rangle_E$ becomes independent on t_E). In this way, it should be possible to find a $t_E \ll t_G$ value that allows to rigorously measure $\langle I(q,t)\rangle_E$.

5 Colloidal glasses are also non-ergodic in nature. Can you analyze the DLS data of colloidal glasses in the same way as that of gels?

Dr. Usuelli : Yes, it is possible to analyze DLS data of colloidal glasses in the same way as in that of gels (using the correction scheme developed by Pusey and Van Megen). Further publications of the two mentioned authors confirm this possibility[5,6]. At the same time, care must be taken in the case when the colloidal glasses are near the glass transition concentration and are therefore marginally non-ergodic. In such a case, the correction scheme developed by Pusey and Van Megen might not work and non-ergodicity needs to be treated through the brute-force method.

6 Are there any considerations that you have to make concerning multiple scattering, especially if your sample is opaque? How would a high concentration of particles in the hydrogel impact the results?

Dr. Usuelli : When multiple scattering is present, DLS measurements are affected, and the extracted information is not reliable anymore. Therefore, there are two strategies that could be followed.

The first one is to increase on purpose the opaqueness of the sample until it becomes turbid, and each photon gets scattered multiple times. In such a context, the behavior of the photons in the sample could be described as a random walk and the scattering functions can be described through the formalism of Diffusing Wave Spectroscopy (DWS). LS Instruments designs a dedicated instrument for performing DWS measurements (the DWS RheoLab), which automatically takes non-ergodicity into account through echo-measurements based on a rotating glass.

The second strategy is to perform the measurements with designated geometries (two-color DLS, 3D DLS) that allow to correct for multiple scattering and to extract therefore only single scattering information. The mentioned methods, because of the correction, also introduce a reduction in the intercept of the measured intensity correlation functions: therefore, non-ergodicity and multiple scattering correction need to be blended with rigorous theoretical treatments, which were developed in the literature[7–9].

7 If the gel I am looking at is highly inhomogeneous (e.g. large pores in which very small, polydisperse, objects can diffuse almost freely), could I be tricked in considering the system non-ergodic, while I am simply looking at different diffusion times?

Dr. Usuelli : When an arrested structure (which is non-ergodic) coexists with polydisperse objects which can diffuse almost freely (and are therefore ergodic), the scattering properties of the considered sample contain both contributions. However, it has to be expected that the measured intensity correlation function depends on the scattering properties of each contribute.

If the network scatters so strongly, that masks the scattering from the freely diffusing objects, the measured intensity correlation function would (highly probably) show non-ergodic features (such as reduced intercept, that changes as a function of the measured sub-ensemble). On the other hand, if the freely diffusing colloids scatter much strongly than the surrounding network, it might be that the scattering signal shows almost no hint of non-ergodicity and reflects instead the free diffusion of the colloidal units.

A more detailed answer to this question would require a deeper knowledge of the sample of interest.

8 Can you extract information about the thickness of the stands of the polymer, not only the mesh size?

Dr. Usuelli : In the presented study, the mesh size of amyloid fibril gels was extracted from the plateau value of the intermediate scattering function. The motion of the amyloid fibrils was described through the formalism of semi-flexible polymers; previous studies showed that, from the time-dependence of the intermediate scattering function of semi-flexible polymers, it is also possible to extract other quantities of interest (such as the thickness of the strands of the polymers, and their persistence length)[10].

As a general hint, once the intermediate scattering function is extracted through a rigorous treatment of non-ergodicity, its behavior can be modeled as a function of the system of interest (many theoretical analyses can be found in the literature). Such an analysis typically allows extracting parameters of interest from the studied sample.

9 Is there any requirement on the color of the sample?

Dr. Usuelli : For light scattering experiments, one would ideally measure transparent samples, that show no/little absorption in the visible range of light. When the sample turns opaque/turbid (and therefore white in color), the considerations shared in answer 6) enable a rigorous treatment of the sample. However, when the sample of interest shows specific colors as a consequence of the absorption of light, the best way to proceed would be to perform a UV-Vis characterization of the sample of interest, in order to determine its absorption coefficient as a function of the wavelength of light. Then, the absorption coefficient of the sample at the wavelength of the used laser source could be checked. If the sample shows little/no absorption at the wavelength of interest, it is possible to treat the DLS data as usual. Otherwise, if the absorption of the sample is not negligible, one needs to apply special correction schemes that take the absorption-induced local heating into account.

10 Which measurement angle is ideal to characterize mesh size in gels?

Dr. Usuelli : The measurement angle, together with the wavelength of the laser and the refractive index of the solvent, determine the probed q-vector (q), which is in turn associated with a characteristic probed length-scale ($\delta \sim 2\pi/q$). In the case of amyloid fibril gels, the probed length scale should be smaller than the mesh size (ξ_m), to probe the dynamics of single filaments (and to allow therefore a rigorous theoretical treatment)[10]. While this holds true for gels made from semi-flexible fibrils, the characterization of other systems might have different requirements, in terms of the comparison between the probed length scale $\delta \sim 2\pi/q$ and the relevant length scales that characterize the sample of interest.

11 How do you control the temperature in your instruments?

LS Instruments : Temperature control is achieved using a Peltier system in the NanoLab 3D and DWS RheoLab. In the LS Spectrometer, the sample is immersed in an index-matching liquid bath coupled to an external temperature circulator.

12 What is the wavelength of the laser radiation used in the LS Spectrometer?

LS Instruments : The wavelength of the laser used in the LS Spectrometer is 638 nm.

13 When will the CORENN method be available on the LS Spectrometer?

LS Instruments : We released LsLab for the LS Spectrometer in early 2022, which includes CORENN analysis: please get in touch with us if you would like an update of your software!

References

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